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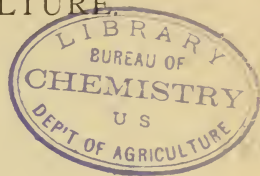
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BULLETIN No. 47.

U. S. DEPARTMENT OF AGRICULTURE.
DIVISION OF CHEMISTRY.



PROCEEDINGS

OF THE

TWELFTH ANNUAL CONVENTION

OF THE

ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS,

HELD AT

WASHINGTON, D. C.,

SEPTEMBER 5, 6, AND 7, 1895.

EDITED BY

HARVEY W. WILEY,
SECRETARY OF THE ASSOCIATION.



WASHINGTON:
GOVERNMENT PRINTING OFFICE.

1896.

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LETTER OF TRANSMITTAL

U. S. DEPARTMENT OF AGRICULTURE,
DIVISION OF CHEMISTRY,
Washington, D. C., November 1, 1895.

SIR: I beg to transmit herewith for your approval the manuscript of the proceedings of the twelfth annual meeting of the Association of Official Agricultural Chemists, and ask that it be printed as Bulletin No. 47 of the Division of Chemistry.

H. W. WILEY,
*Chief of the Division of Chemistry, and
Secretary of the Association of Official Agricultural Chemists.*

Hon. J. STERLING MORTON,
Secretary of Agriculture.

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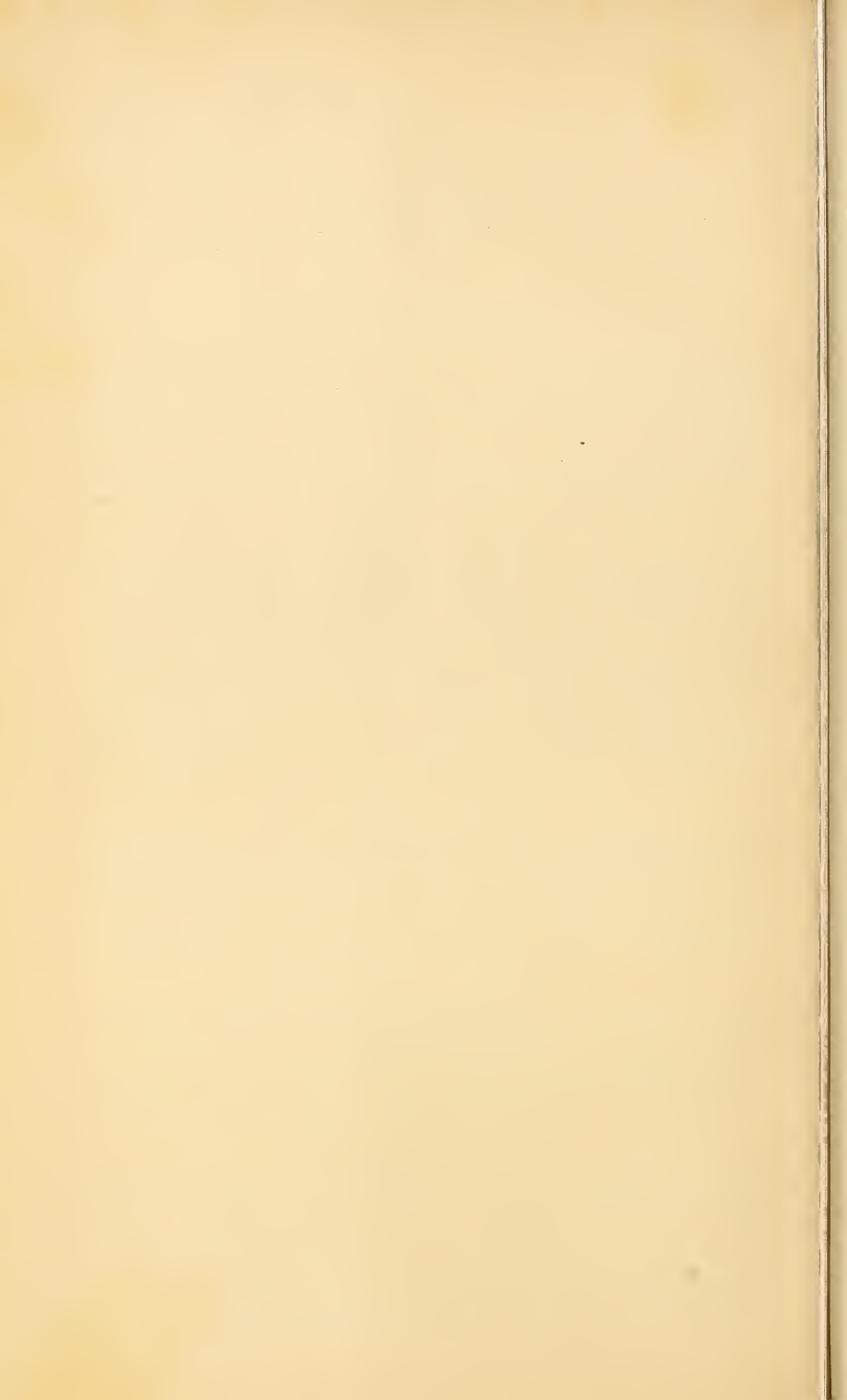
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PROCEEDINGS OF THE TWELFTH ANNUAL CONVENTION OF OFFICIAL AGRICULTURAL CHEMISTS OF THE UNITED STATES.

FIRST DAY.

THURSDAY—MORNING SESSION.

The convention was called to order at 10 o'clock by the president, Mr. H. A. Huston, in the lecture room of the National Museum.

The PRESIDENT. I believe it is the custom to appoint two committees at the sessions of this association, one a committee to invite the Secretary and Assistant Secretary of Agriculture to attend the meetings, and I will ask Mr. Gaines and Mr. Stubbs to serve on that committee. The other is upon the order of business, and I will ask Messrs. Rawls, Winton, and Goss to act on that committee.

MEMBERS AND VISITORS PRESENT.

President, H. A. Huston, State Chemist of Indiana, La Fayette, Ind.
Vice-President, B. B. Ross, State Chemist of Alabama, Auburn, Ala.
Secretary, H. W. Wiley, Chief of Division of Chemistry, United States Department of Agriculture, Washington, D. C.

Alexander, J. P., Division of Agricultural Soils, United States Department of Agriculture, Washington, D. C.

Anderson, James T., Agricultural Experiment Station, Auburn, Ala.

Bartlett, J. M., Chemist Maine Experiment Station, Orono, Me.

Beal, W. H., Office of Experiment Stations, United States Department of Agriculture, Washington, D. C.

Benjamin, Marcus Mitchell, New York.

Bigelow, W. D., Division of Chemistry, United States Department of Agriculture, Washington, D. C.

Bornberger, F. B., Maryland Agricultural College, College Park, Md.

Brown, W. G., Division of Chemistry, United States Department of Agriculture, Washington, D. C.

Carr, Oma, Division of Chemistry, United States Department of Agriculture, Washington, D. C.

Chestnut, V. K., Bureau of Animal Industry, United States Department of Agriculture, Washington, D. C.

Crampton, C. A., Treasury Department, Washington, D. C.

Croxton, H. E., Donaldsonville, La.

Cutter, W. P., late Chemist Utah Station, Librarian United States Department of Agriculture, Washington, D. C.

Davidson, R. J., Virginia Agricultural Experiment Station, Blacksburg, Va.

- Dorset, Marion, United States Department of Agriculture, Washington, D. C.
- Dugan, John, Division of Chemistry, United States Department of Agriculture, Washington, D. C.
- Ewell, E. E., Division of Chemistry, United States Department of Agriculture, Washington, D. C.
- Frear, William, Agricultural Experiment Station, State College, Pa.
- Fries, J. A., Agricultural Experiment Station, State College, Pa.
- Gaines, Richard H., State Chemist of Virginia, Richmond, Va.
- Gardner, F. D., Division of Agricultural Soils, United States Department of Agriculture, Washington, D. C.
- Goss, Arthur, Mesilla Park, N. Mex.
- Heavener, J. G., Division of Agricultural Soils, United States Department of Agriculture, Washington, D. C.
- Herff, B. von, 93 Nassau street, New York.
- Hite, B. H., Morgantown, W. Va.
- Hutchinson, W. L., Chemist State Agricultural College, Agricultural College, Miss.
- Kedzie, R. C., Michigan Agricultural Experiment Station, Agricultural College, Mich.
- Kilgore, B. W., Raleigh, N. C.
- Krug, W. H., Division of Chemistry, United States Department of Agriculture, Washington, D. C.
- Lindsey, J. B., Hatch Experiment Station, Amherst, Mass.
- McDonnell, C. C., College Park, Md.
- McDonnell, H. B., State Chemist, College Park, Md.
- McDonnell, M. E., Pennsylvania Experiment Station, State College, Pa.
- McDowell, M. S., State College, Pa.
- McElroy, K. P., Division of Chemistry, United States Department of Agriculture, Washington, D. C.
- Manns, A. G., Chemist, Armour & Co., Chicago, Ill.
- Merrill, L. H., Orono, Me.
- Mitchell, A. S., Chemist, Wisconsin Dairy and Food Commission, Milwaukee, Wis.
- Moore, Charles C., jr., Division of Chemistry, United States Department of Agriculture, Washington, D. C.
- Morse, F. W., Durham, N. H.
- Myers, John A., Director Agricultural Experiment Station, Morgantown, W. Va.
- Patterson, H. J., Agricultural Experiment Station, College Park, Md.
- Patterson, L. G., Washington, Pa.
- Payne, George F., State Chemist, Atlanta, Ga.
- Peacock, S., Editor American Fertilizer, Philadelphia, Pa.
- Penny, C. L., Newark, Del.
- Persons, A. A., Florida Agricultural College, Lake City, Fla.
- Peter, A. M., Kentucky Agricultural Experiment Station, Lexington, Ky.
- Rawls, W. A., Tallahassee, Fla.
- Rosell, C. A. O., United States Patent Office, Washington, D. C.
- Runyan, E. G., Division of Chemistry, United States Department of Agriculture, Washington, D. C.
- Sanborn, T. F., Division of Chemistry, Spreckelsville, Maui, Hawaiian Islands.
- Sherman, H. C., Maryland Agricultural College, College Park, Md.
- Skinner, W., Maryland Agricultural College, College Park, Md.
- Street, J. P., Agricultural Experiment Station, New Brunswick, N. J.
- Stubbs, W. C., Director Louisiana Experiment Stations, Audubon Park, New Orleans, La.
- Tassin, Wirt, United States National Museum, Washington, D. C.
- Terne, Bruno, Philadelphia, Pa.
- Trescott, T. C., Division of Chemistry, United States Department of Agriculture, Washington, D. C.

Van Slyke, L. L., Agricultural Experiment Station, Geneva, N. Y.
 Veitch, J. P., Maryland Agricultural College, College Park, Md.
 Westenfelder, B. D., American Oak Leather Company, Cincinnati, Ohio.
 Wheeler, H. J., Chemist, Rhode Island Experiment Station, Kingston, R. I.
 Whitney, Milton, Chief Division of Agricultural Soils, United States Department of
 Agriculture, Washington, D. C.
 Wilkinson, J. F., Capitol Building, Atlanta, Ga.
 Willits, Edwin, Washington, D. C.
 Winton, A. L., New Haven, Conn.
 Wolff, jr., Frank A.
 Woods, C. D., Middletown, Conn.

ADDRESS OF THE PRESIDENT.

GENTLEMEN OF THE ASSOCIATION: The experience of the last few meetings of this association indicates the advisability of consuming as little time as possible in listening to any preliminary remarks by the presiding officer. Too much work has been crowded into our final sessions, and throughout our meetings it has often happened that the lack of time has led some to present papers by title only. A paper so presented can not be properly discussed, and while such a proceeding saves time it defeats the object of the second section of article 1 of our constitution, which is to afford an opportunity for discussion of matters of interest to agricultural chemists.

The opportunity for discussion is an important element in securing a satisfactory attendance at our meetings, and it should not be unnecessarily abridged. If the association is to maintain its influence, time must be given for the consideration of every important fact having a direct bearing on our work.

The association has always been ready to improve its organic law, as expressed in its constitution, whenever such changes seemed demanded. It is suggested that the second paragraph of article 4, which now requires all reporters to send out samples, standard reagents, and reports blanks, should be so amended as to make these acts discretionary with the reporters, as in certain lines of work it has been found unprofitable and well-nigh impossible to distribute samples.

Article 6 provides that the annual meeting of the association shall be held at such place as shall be decided on by the association. I can find no record of any action by the association locating a meeting. The meetings have been called by the executive committee, and it may be well to change the article to make such a call regular in case the association does not desire to locate the next meeting before adjourning.

Article 7, relating to changes in methods of fertilizer analyses, requires such changes to be made by unanimous consent, unless an opportunity has been given to all fertilizer control chemists to test the proposed changes. The question has arisen whether such changes must have been proposed at a meeting of the association, or whether it will be considered that a notice from a reporter or member to the other members of the association shall be considered as giving the required

opportunity. It might be well to settle this matter at once, so that reporters and members will know how to proceed in case changes are found desirable. The point here made may, at first sight, seem one of minor importance; but the past history of the association shows that article 7 of the constitution was adopted none too soon. We must keep in mind that the first object in change of method is to obtain accuracy within reasonable limits. However attractive time and labor saving methods may be to the busy analyst, the association must not let these considerations outweigh considerations of correct methods of work. The reputation of the association requires that the methods that obtain its sanction should be as nearly correct for the purposes for which they were devised as the present state of science will permit.

The work of investigators of methods of analysis necessarily leads them into matters of minute detail. We sometimes get so close to our work as to narrow our horizon, and for the time being lose sight of broader fundamental principles.

The question of "available" phosphoric acid has occupied a large share of the attention of this association in the past, and must do so in the future. The methods of analysis of phosphates have been changed repeatedly. After a careful consideration of the subject, I am of the opinion that one of the best courses of training for one contemplating a proposition to change the methods of analysis of phosphates is to read all the proceedings and papers of this association relating to phosphates, including the proceedings of the Atlanta convention of May 15 and 16, 1884.

Recent work would seem to indicate that a distinction will have to be made between the available in real superphosphates and in non-acidulated goods, and that, in order to make laboratory determinations a reliable indicator of field results, different methods may have to be applied to the different classes of goods.

While there seems no pressing necessity for an immediate change in the method for determining available phosphoric acid, the fact that new forms of phosphates are constantly coming on the market requires us to investigate the laboratory and field behavior of these substances with a view of ascertaining proper methods of valuing them when they come to us either alone or in mixed goods.

A young lady recently returned from the blue-grass region, on being asked for her impression of the State, said that it seemed to be a place where they educated their horses and let the men just grow up. This association seems to be in a somewhat analogous position on the food question. For, while our reports abound in researches on food for live stock, the only work on the food for man is represented in the reports on dairy products and sugar, and as a rule comparatively few of us contribute to either of these branches. Even the question of hotel accommodations was referred to committee on fermented and distilled liquors.

Our constitution was revised in 1885 so as to include in our membership municipal chemists, whose duties include inspection of very many articles of human food. The association might extend its usefulness by giving some attention to the subject of the examination of many kinds of human food, which we all know will hardly bear close scrutiny. Possibly the elaborate and very valuable work done by the Division of Chemistry of the Department of Agriculture has seemed so complete that it seems unnecessary for the rest of us to direct much attention to the subject. But it is possible that if this association, with its membership representing all parts of the country, should have an able committee considering the matter, it might afford technical assistance and strong moral support to the municipal chemist struggling to do honest work, often in conflict with alleged experts, and also exert a restraining influence on some whose work is sometimes tainted with sensationalism.

The question of what substances may be considered as proper preservatives of food materials is daily becoming of more importance, and as very many of us are called to pass on the matter in our work it would be of great assistance to have some expression of this association in regard to the matter. The reckless manner in which all sorts of substances are added to food material, either to prevent fermentation or to conceal bad quality, merits our serious consideration.

The association is to be congratulated on the willingness of its members to abandon a position already assumed when new facts are brought to light requiring a change of view. The future strength of the association depends in no small degree on a continuance of this attitude.

At our last meeting it was voted to create a new committee to act on the recommendation of reporters for changes in the methods of analysis, and on this committee I will ask Messrs. Lindsey, Peter, Patterson, and Wheeler to serve. I believe it is understood that the reporter whose recommendation is under consideration shall meet with that committee. It seems impracticable to draw out his reasons for the recommendations he makes in any other way.

The business of the association can hardly proceed, I think, until we have some report from the committee upon the order of business.

MR. MYERS. I move that a recess of fifteen minutes be taken to allow the committee to consider the matter and prepare a report.

A recess of fifteen minutes was taken.

THURSDAY—AFTER RECESS.

THE PRESIDENT. The following is the committee's report for the order of business: First, report on potash; second, report on food and feeding stuffs; third, soils and ash; fourth, phosphoric acid; fifth, report of abstract committee; sixth, fermented and distilled liquors; seventh, nitrogen; eighth, dairy products; ninth, sugars. Election of officers to

be the special order for Friday, the 6th, at 3 p. m. Hours of meeting, 9.30 a. m. to 12.30 p. m; 1.30 p. m. to adjournment.

The report of the committee was adopted.

The PRESIDENT. I would like to ask the visiting chemists and members connected with the industries in which our work is of interest to be present with us and register, and to take part in the discussions. I would also call attention to the fact that municipal chemists charged with the control of food products are eligible to membership in this association.

At this moment the Secretary of Agriculture entered the hall.

The PRESIDENT. The Secretary of Agriculture is present, and I know you will be glad to see him and hear any remarks which he will be kind enough to make. I have the honor to introduce the Honorable Secretary of Agriculture.

REMARKS OF SECRETARY MORTON.

MR. PRESIDENT AND GENTLEMEN OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS: I was rather unexpectedly drafted into this position by Dr. Kedzie and Dr. Stubbs. I should much prefer to have had the Assistant Secretary of Agriculture, Dr. Charles W. Dabney, jr., here instead of myself. The truth is, I have not been in the habit of appearing before chemists conducting original investigations. My line of life, pioneering the transmissouri country in Nebraska since 1854, frequently brought me in antagonistic contact with some of those Indians whose portraits you see hanging about on the walls of this room. And although they made *aboriginal* biological investigations instead of original, I should not be as nervous in speaking at an Indian council as I am before your body of original research. However, I must welcome you, gentlemen, as the forerunners of that time when the farmer, like the lawyer and the physician, shall be educated for his profession. I do believe that, with the intense competition in all the markets of the world for the sale of farm products, the time is not distant when it will be considered as perfectly absurd for a man to undertake farming except scientifically, and with a thorough knowledge of chemistry as applied to agriculture, and of nearly all the sciences applicable to agriculture, as it would be for an individual to attempt the practice of any profession without having taken a special course therefor.

The farmers of the United States now need more markets rather than more crops. Information comes from Russia to the effect that their wheat crop is simply enormous, and (as I showed Dr. Kedzie yesterday) a letter written me on the 13th of last month by the agent of the McCormick manufacturing establishment located at Odessa states that they thrash frequently 75 bushels of wheat from a single acre in Russia. And in that Empire much of the wheat of 1893 is still in stack unthrashed, awaiting better markets in Europe.

From Argentina a letter dated the 17th of last month declares equal

competition in the wheat markets of the world and likewise in the cattle markets of Europe. Argentina shipments of cattle this year, it is estimated, will amount to 260,000 head of live animals, to say nothing of refrigerated meats. Thus it is absolutely necessary that American farmers be educated in all that appertains to the science of agriculture in order that they may successfully meet this intense competition the world over. In view of these facts, the experiment stations in the several States and Territories are, no doubt, the most potent influences to properly prepare American farmers for this contest as to markets. The strife between the commercial nations of the earth is to see who shall most feed and most clothe mankind. We are all brothers in this great, tumultuous, peaceful contention. We are all Cains and Abels making offerings of our products. This contest is now growing everywhere closer and closer and more intense, and therefore it is safe to say that the agricultural producers who are best equipped, best educated by experiment stations, scientific men, and original investigations, will nearest win and hold the world's markets.

The experiment stations are, by a permanent appropriation, maintained with the agricultural colleges out of the money in the United States Treasury from the sale of public lands not otherwise appropriated. The time is not distant when there will be no money in the Treasury of the United States from the sale of public lands. Then each State will undoubtedly have to take care of its own experiment station out of its own treasury.

The experiment stations have for me a very attractive side, for I think through them all new, rare, and improved varieties of seeds should be tested, and that any appropriation that the National Government may determine to make hereafter for the introduction of new and improved varieties should be made directly to the experiment stations, for the reason that these stations, in charge of men educated particularly for that purpose, will best know what to try in each environment and soil. I think it quite possible that in the near future such seed appropriations, if made at all, may be made to the stations. Then seeds imported will be sent directly to each of the stations. Then through their scientific handling and examination, we shall avoid the distribution of such pests as the Russian thistle and other vicious exotics which we have brought in heretofore in unexamined seeds, which at a great cost have been promiscuously scattered over the country.

Gentlemen, I heartily welcome you to the Department of Agriculture, and assure you that Dr. Dabney and myself will in every possible lawful manner do all we can to entertain you and to promote the vast and vital interests permanently which you are charged to conserve.

Mr. STUBBS. The committee appointed to invite the Secretary and Assistant Secretary would desire to make a supplementary report that the Assistant Secretary was invited, but he was so busy he could not attend. He sends his regrets.

At the conclusion of the Secretary's remarks, Mr. Wheeler read the report on potash.

REPORT ON POTASH.

By H. J. WHEELER, *reporter*, and A. L. WINTON, *associate reporter*.

On November 17, 1894, a circular letter asking for cooperation in the potash investigation for 1895 was sent to over fifty American chemists, and a favorable response was received from twenty-one. Thirty-one sets of material were sent out on January 23, 1895, including ten for distribution among foreign chemists.

Only eleven reports were received in season for tabulation and incorporation in this report.

The outline of the work and directions for the same are embodied in the following circular letter which accompanied the sample:

KINGSTON, R. I., *January 23, 1895.*

DEAR SIR: I send you to-day by express for the work on potash for the A. O. A. C., two bottles of material. One contains a sample of potassium chlorid and the other a solution of "impurities" containing sulphuric acid, hydrochloric acid, phosphoric acid, nitric acid, lime, magnesia, soda, and organic matter in form of cane sugar. In the preparation of the "impurities" only so-called c. p. reagents were employed. Larger quantities of phosphoric acid and sulphuric acid have been introduced in the "impurities" than in those of 1894.

AMOUNT OF KCl TO BE USED IN THE TEST.

Employ approximately 0.5 of a gram of KCl salt in each test. Pour out the salt from the rubber stoppered bottle, ascertaining the exact weight of salt used by difference; or transfer the entire amount of KCl to a tight weighing bottle at the outstart, and proceed then in a similar manner. It is important that the same quantity of PtCl₄ solution be employed in each test, and for this reason it would be advisable to use the balance as a guide in pouring out the KCl, so that approximately 0.5 of a gram will be secured in each case. Do not attempt to weigh out exactly 0.5 of a gram.

A.—Tests by alternate method (Proceedings Eleventh Annual Convention A. O. A. C., p. 350):

- (1) Employ approximately 0.5 gram of KCl and 20 cc of the impurities.
- (2) Employ 20 cc of the impurities.
- (3) Employ distilled water, using the same amounts of BaCl₂ and Ba(OH)₂ as in (1) and (2), and as much (NH₄)₂ CO₃ as necessary.
- (4) Evaporate the solution of the KCl with PtCl₄ solution, and finish the test as above.
- (5) Evaporate same amount of PtCl₄ as employed in the above tests, without KCl, and finish the test as above.

B.—Tests by Lindo-Gladding method (Proceedings Eleventh Annual Convention A. O. A. C., p. 349):

- (1) Take approximately 3 grams of the KCl and 120 cc of the impurities, and dilute the mixture somewhat, yet not so much as not to allow of the addition of the necessary ammonia and ammonium oxalate (which are to be added to the hot solution), so that the whole can finally be made up to 300 cc after cooling. Filter through a dry filter, and employ 50 cc of this solution in each case for the completion of each test.
- (2) Take 120 cc of impurities and enough distilled water so that the heated solution will be of about the same volume as in (1); add ammonia and ammonium oxalate and proceed as in (1).
- (3) Add to the ammonia and ammonium oxalate sufficient distilled water to equal 300 cc; then take 50 cc of this solution and proceed as in (1) and (2).
- (4) Evaporate a solution of 0.5 of a gram of KCl with PtCl₄ solution, and finish the test as above.
- (5) Evaporate the same amount of PtCl₄ solution as employed in the above tests, without addition of KCl, and finish the test as above. Test in addition, if you can, the use of CaCl₂, as suggested by Huston. (Proceedings Eleventh Annual Convention A. O. A. C., p. 26.) Consult results by De Roode in this connection (Jour. Am. Chem. Soc., Vol. XVII, No. 1, Jan., 1895, p. 46):

Moisture test.—The samples sent out are uniform in moisture, and if the samples are handled as directed the tests by the reporters will be used for reduction to a dry basis.

Directions.—Omit washing with ether in the alternate method. By an oversight of the reporter for 1894 this was not left out of the method, as it should have been. At the outstart make sure that you have enough of each of the reagents on hand so that the same lot may serve for all of the tests. In the case of each method use the same amounts of reagents for all of the tests given under that method (excepting test (3) under A, as there specified), and to this end make tests (1) under each method at the outstart, to determine the amount of reagents required. Owing to the difference in the methods and the fact that in that of Lindo-Gladding the amount of potash must be measured in solution by a pipette, instead of directly by weight, as by the alternate method, a test of the measuring flask and pipette employed should be made as follows: Take approximately 3 grams of KCl, the exact weight of which is determined by difference, dissolve and make up to 300 cc and evaporate an aliquot part, using the same flask and pipette as above indicated. Heat until absolutely dry, and weigh. Report the weight of KCl employed and that finally obtained. For the sake of perfect uniformity in the work, please follow strictly the methods as laid down by the A. O. A. C. (except where they conflict with those given), taking especial care when evaporating with PtCl_4 solution to remove from the water bath just as soon as the point is reached at which the material will entirely crystallize upon cooling. Do not allow the solution to come to dryness on the water bath. If not convenient to treat with alcohol at once, place in a desiccator, to prevent absorption of moisture. In regard to the treatment with 80 per cent alcohol, we would advise the following method: When cool, add about 30 cc of alcohol, pulverize the salt, and let stand about twenty minutes with frequent stirring, decant on filter, wash by decantation with successive portions of about 10 cc of alcohol, allowing each portion to remain in contact with the salt for about two or three minutes, stirring frequently. Complete the washing as directed in the proceedings of the A. O. A. C., excepting the use of ether, as above mentioned. Do not collect two or more precipitates upon the same filter, but prepare a new Gooch filter for each precipitate, washing with the same solutions as used subsequently. Dry in water bath to constant weight. The solution to which the PtCl_4 solution is added should amount to about 50 cc in each case.

If, upon the completion of all the work outlined above, you have sufficient material and time, we would suggest that you make additional tests by either the barium oxalate method of Schweitzer and Lungwitz (*Chem. Zeit.* Aug., 1894, p. 1320), or that of Garrigues (*Jour. Am. Chem. Soc.*, Vol. XVII, Jan., 1895, p. 47). If you desire to try comparative tests by these methods, the reporter will furnish directions for procedure upon application, so that the work may be conducted in a uniform manner, and thus be comparable with other results. Additional quantities of impurities can be furnished if desired. Report weights of KCl used and of K_2PtCl_6 obtained by July 1. Avoid deviating from the directions, but, if forced to, state all details relating thereto.

H. J. WHEELER, *Reporter.*

A. L. WINTON, *Asst. Reporter.*

The following chemicals were used in the preparation of 40 liters of the above-mentioned impurities:

- 240 grams c. p. tricalcic phosphate.
- 344 grams c. p. sulfuric acid 1.84 sp. gr.
- 262 grams c. p. magnesium chlorid.
- 164 grams cane sugar.

The sulfuric acid was allowed to act upon the tricalcic phosphate first in concentrated solution. It was then almost fully diluted and allowed to stand some days with frequent agitation, the remaining ingredients were then added, the solution was passed through a filter, and sterilized when bottled.

Twenty cubic centimeters of the above solution (the amount employed in each determination) was found to contain the following:

Calcium oxid	0.0198
Magnesium oxid0245
Sodium oxid.....	.0304
Phosphoric acid (P_2O_5).....	.0484
Sulfuric acid (SO_3).....	.2249

The amount of calcium oxid is about one-third of that present in the impurities used in 1894, the magnesium oxid practically the same, the phosphoric acid slightly less, and sulfuric acid about six times as great.

The following table shows the results reported by the individual chemists:

TABLE A.—*Results of potash work for 1895 as received—Continued.*

Source of analysis.	1 KCl and impurities.				2 Blank impurities and reagents.		3 Blank reagents.		4 Direct evaporation KCl and PtCl ₄ .				5 Blank PtCl ₄ .	
	Alt.		L.-G.		K ₂ PtCl ₆ .		K ₂ PtCl ₆ .		Alt.				L.-G.	
	KCl taken.	K ₂ PtCl ₆ obtained.	KCl taken.	K ₂ PtCl ₆ obtained.	Alt.	L.-G.	Alt.	L.-G.	KCl taken.	K ₂ PtCl ₆ obtained.	KCl taken.	K ₂ PtCl ₆ obtained.	Alt.	L.-G.
New Jersey Station, J. P. Street	500.0	1,629.7	500.0	1,625.6	14.8	13.9	4.2	1.0	500.0	1,623.9	500.0	1,628.6	1.0	0.4
	500.0	1,624.3	500.0	1,624.9	14.0	14.0	3.2	0.6	500.0	1,622.6	500.0	1,627.6	1.0	0.8
	13.3	500.0	1,624.9
New Hampshire Station, E. P. Stone	12.7
	13.8
	499.0	1,630.5	500.0	1,627.5	8.7	13.4
Connecticut Station, A. L. Winton	538.1	1,742.0	500.0	1,634.5	15.0	504.5	1,643.2	504.5	1,643.2	0.0	0.0
	482.6	1,565.6	500.0	1,627.9	10.0	12.8	2.3	0.1	501.0	1,923.0	501.0	1,923.0	0.0	0.0
	507.3	1,642.6	500.0	1,629.9	11.9	14.0	452.0	1,469.2	503.4	1,632.9	0.3	0.3
	500.0	1,633.5	13.3	502.7	1,633.7
	500.0	1,634.4	535.5	1,739.5
	500.0	1,636.0	533.4	1,731.6

DETAILS FROM INDIVIDUAL ANALYSTS RELATING TO DATA IN THE ABOVE TABLE.

A. L. Winton, in the alternate method, after ignition, dissolved in hot water, added a drop of ammonium carbonate, filtered, evaporated, and reignited. The double salt was dried two hours at 100°.

In the Lindo-Gladding method the pipette used for measuring out the aliquot portions was rinsed with water, so as to include any solution which might cling to the sides. Seventy cc of ammonium chlorid wash was drawn through the double salt, which was then washed with 80 per cent alcohol.

W. M. Allen.—In the Lindo-Gladding method the solutions were diluted to 400 cc, and 50 cc were taken. Only 0.3 gram of KCl was used for direct evaporation with PtCl_4 solution. The results were reported as given in Table A.

W. G. Brown reports two nonconcordant results (not tabulated) by the alternate method, supposed to be due to insufficient washing of the precipitate obtained on the addition of barium chlorid and barium hydroxid. In obtaining the results reported, washing was continued until, after acidifying with nitric acid, silver nitrate showed the absence of chlorin. In the Lindo-Gladding method, under test 1, 2.9086 grams of KCl were dissolved in 300 cc of water, and 50 cc taken by measure for each test. Using the same flask and pipette, 3.3540 grams of KCl were made up to 300 cc; two lots of 50 cc each were then measured out, evaporated to dryness, and ignited at low redness, yielding respectively 0.5550 and 0.5557 gram of KCl.

John P. Street employed amounts of KCl approximating 0.5 gram, but calculated them to a uniform basis in reporting.

J. B. Lindsey weighed out exactly 0.5 gram of KCl for his determinations. He also reports that considerable difficulty was encountered in obtaining parallels by the Lindo-Gladding method until washing by decantation was resorted to in lieu of washing on the Gooch filter.

G. William Gray reports that the KCl as employed by him was dried at 140° and the results are reported upon a dry basis. In the Lindo-Gladding method the heating, after adding H_2SO_4 , was conducted in an air bath until charring ensued, and then in a muffle furnace. In the alternate method a similar course of heating was followed, care being taken to keep the muffle furnace just below redness.

F. P. Veitch states that in the Lindo-Gladding method the precipitates were washed with the ammonium chlorid solution four times each by decantation. Attention is called to the lower results in test 1 by the alternate method, supposed to be due to loss by ignition or occlusion, for the precipitates were washed until free from chlorids. He states that the platinum dishes used for three years for the Lindo-Gladding potash determinations are, with one or two unimportant exceptions, uninjured.

W. A. Powers, in testing his flask and pipette, dissolved 4.3798 grams of KCl, and made up the whole to 500 cc. Upon evaporating 50 cc portions and igniting at low redness the following weights were obtained: (a) 0.4331 and (b) 0.4334 gram, which results were used in calculating to a dry basis.

F. H. Wernskiold departed somewhat from the alternate method. Five grams KCl and 200 cc of impurities were dissolved in water, with the addition of 25 cc of 24 per cent HCl, boiled, precipitated with excess of BaCl_2 solution; it was then cooled, neutralized with ammonia, precipitated with ammonium carbonate, made up to 500 cc, and filtered. Of the filtrate 50 cc were evaporated in a platinum dish, the ammonium salts expelled at a low heat; it was then moistened with 2 cc of a saturated solution of oxalic acid, evaporated, and strongly heated. The remainder of the treatment was as with the alternate method, save that the drying was conducted at 105° to constant weight (a), and the precipitate was dissolved in hot water and the crucible dried and again weighed (b). The results were reported as follows: $(a-b) \times 0.193 = \text{potash}$. Potash (K_2O) found = 61.83 per cent.

B. L. Hartwell reported his results under 1 and 4 calculated to the basis of 1 gram

of KCl in its natural state. In the test of the flask and pipette used in the Lindo-Gladding method the following data were given:

Fifty cc of a solution of 3.0675 grams of KCl in 300 cc water yielded upon evaporation and heating 0.5081 gram, and in a second test 50 cc of a similar solution of 4.1486 grams yielded 0.6870 gram, which results were used in reducing the Lindo-Gladding results to a dry basis.

TABLE B.—*Summary of results derived from Table A.*

Source of analysis.	1-2 KCl and impurities (1) minus blank for impurities and reagents (2).		4-5 Direct evaporation KCl and PtCl ₄ (4) minus blank for PtCl ₄ (5).	
	Alt.	L.-G.	Alt.	L.-G.
	Per cent KCl.	Per cent KCl.	Per cent KCl.	Per cent KCl.
Illinois Station, W. A. Powers	¹ 96.14	99.89	¹ 99.02
	¹ 96.87	99.48	¹ 99.56
Rhode Island Station, B. L. Hartwell	98.71	100.57	99.67	99.60
	100.74	99.72	99.57
		99.67
		99.74
West Virginia Station, G. Wm. Gray	98.23	98.78	¹ 99.06	¹ 99.06
	97.77	98.78	¹ 98.97
	98.09	98.95
	98.15
Maryland College, F. P. Veitch	¹ 102.07	98.46	99.53	99.87
	¹ 95.90	98.61	99.92	99.85
	98.28	100.02
North Carolina Station, W. H. Allen	99.20	99.65
	99.12	99.63
	99.34	99.53
Massachusetts Station, J. B. Lindsey	97.80	98.33	99.77	99.63
	97.79	98.29	99.75	99.55
United States Department of Agriculture, W. G. Brown	² 98.86	100.20	100.00	² 99.76
	98.77	100.41	99.89	99.74
	² 98.62	100.41	99.63	² 99.67
	98.59	100.31	99.63
New Jersey Station, J. P. Street	99.18	98.98	99.93	99.67
	98.84	98.94	99.87	99.59
	99.70
New Hampshire Station, E. P. Stone	¹ 99.76	99.01	99.99	99.99
	99.44	99.89	99.89
Connecticut Station, A. L. Winton	98.71	99.48	99.75	99.57
	98.85	99.53	99.73
	98.69	99.63	99.70
	99.64
Christiania, Norway, Chemical Control Station, F. H. Werm- skjold	³ 98.35
Maximum	99.18	100.57	100.02	99.99
Minimum	97.77	98.28	99.53	99.53
Average (factor 0.3056)	98.44	99.35	99.79	99.63
Average (At. Wt. Pt = 195)	98.85	99.77	100.21	100.10

¹ Omitted from averages owing to wide departure from other results.

² Dried for half an hour only and omitted in calculating averages; the results immediately following are from constant weights.

³ Omitted from average owing to a modification of the alternate method.

In calculating the results in the foregoing table to a dry basis, except where otherwise specified, the percentage of moisture as determined by Ogden and Winton, of the Connecticut Station, viz, 0.45 per cent, was employed. In consideration of the manner of weighing the portions of pure KCl for determination the results ought to be better for comparative purposes than in 1894, when another system was followed. Notwithstanding this consideration, however, a great amount of individuality is still apparent in the results, doubtless due in a few cases to lack of skill in manipulation by the one or the other method. In the tests by direct evaporation, the results are, as they were last year, slightly lower by the Lindo-Gladding than by the alternate method, showing, even if the entire discrepancy were attributed to double decomposition, that the error amounted to but 0.11 per cent of KCl, even when 0.5 gram of pure salt was employed for a test; so that in the case of ordinary determinations where one has to deal with smaller quantities of double salt, the error from this cause must be inconsiderable, showing that the method is not open in this respect to the serious criticism which it has received at the hands of Breyer and Schweitzer. In considering the data secured in determining potash in the presence of impurities, the results this year are in strong contrast to those of last year, viz, in 1894, 0.4 per cent more KCl was recovered by the alternate than by the Lindo-Gladding method, while this year an average of 0.91 per cent more was recovered by the latter method than by the former. It will be noticed that the great difference in the impurities is in the amount of H_2SO_4 present, so that the results point strongly to the conclusion that a greater amount of occlusion must have resulted in the case of the alternate method, or that the double salt from the Lindo-Gladding method contained a greater amount of impurities. It is evident, therefore, that the Lindo-Gladding has given, under the conditions of the trial, more nearly accurate results than the alternate, due either to a more satisfactory compensation of errors or to the inherent virtue of the method. Considering the results of both years, it appears that in the absence of considerable quantities of sulfates the alternate may give equally good if not better results than the method of Lindo-Gladding, but that where much H_2SO_4 is to be removed the preference must be given to the latter method.

Comparing the potash recovered by the Lindo-Gladding method in the presence of impurities with that obtained by the direct evaporation and washing with 80 per cent alcohol, it will be seen that the loss of potash, even by this method, averages 0.44 per cent, due to occlusion, ignition, or other causes.

Undoubtedly, some of the difficulties of individual analysts were due to the fact that one of the methods was new to them, and they had not acquired the requisite skill in the particular manipulation required; two in particular report very unsatisfactory results, and one chemist withheld all his data on that account. One report states that by the alternate method results 10 per cent too low were obtained in one test by expelling the ammonium salts in an open platinum dish "below a red heat." Yet those familiar with the method and the proper manipulation never meet with such discrepancies, on which account it appears probable that the heating must have been carried on at too high a temperature, perhaps in direct sunlight, under which circumstances the dish may easily have been overheated without its being observed. These results are mentioned for the purpose of emphasizing the importance of intrusting to trained analysts such work as is intended to furnish data of scientific value, rather than to use the material as a part of the outfit of a chemical gymnasium for beginners.

The amounts of double salt recovered from the blanks with reagents show, as did those of last year, that considerable errors may be made if such blanks are omitted in potash work; and that the work of N. Robinson and Breyer and Schweitzer, who made no blanks on the reagents employed in the recovery of potash lost by occlusion, double decomposition, and in other ways, instead of serving as a satisfactory basis for a criticism of methods, is of itself open to the severest criticism, especially in view of the fact stated in last year's report that 7 grams of $\text{Ba}(\text{OH})_2$ and large quantities of other reagents were employed by Breyer and Schweitzer in a single test for the recovery of potash.

MISCELLANEOUS DATA BEARING UPON POINTS DISTINCT FROM THE COMPARISON OF METHODS.

(A) *Is drying for half an hour sufficient?*

W. G. Brown found that the double salt from approximately 0.5 gram, after drying in a steam bath for half an hour, lost in each of four determinations 1.7, 0.4, 0.4, 0.6 milligrams, respectively, when subsequently heated at 100° to constant weight. F. P. Veitch found under corresponding conditions that the double salt obtained in three tests lost upon heating for half an hour longer at 120° 0.0, 0.7, and 1.3 milligrams, respectively. From the foregoing results the error due to drying but half an hour ranged approximately from 0.05 to 0.10 per cent of KCl, which was probably less than otherwise, owing to the fact that the final precipitation was made from a dilute solution, under which circumstances the drying has been found by Winton¹ to progress more rapidly. In fact, it was due to the results already obtained by Winton that directions for precipitation under such conditions were given in the circular of instructions rather than ad libitum, or from a concentrated solution according to Fresenius.

(B) *On the use of $MgCl_2$ in place of $CaCl_2$, as suggested by Huston, in connection with the Lindo-Gladding method.*

B. W. Kilgore, in forwarding the results obtained by W. M. Allen, states that since the mention by Huston at the last meeting of the A. O. A. C. about adding calcium chlorid, and the statement of De Roode in the American Chemical Journal² that it did not accomplish the object intended, we have made some investigations in the same line by substituting magnesium chlorid just after precipitating with ammonia and ammonium oxalate and allowing it to stand one to two hours, or long enough for any phosphate that might be present in solution to be precipitated. One cc of a saturated solution of magnesium chlorid was added for this purpose. He further states that the washing of the K_2PtCl_6 is easier and rendered more complete by this modification. This procedure suggested itself from an examination of the insoluble residue obtained after dissolving precipitates of K_2PtCl_6 in hot water, which showed it to consist mostly of iron phosphate with some calcium phosphate, and, so far as their observations extend, the use of magnesium chlorid eliminates this error. As the impurities sent out did not contain iron, a small amount was added in a few determinations. Owing to a misunderstanding, less than 0.5 gram of KCl was employed in the tests, by which, as stated, the errors of analysis may have been multiplied. The following are the results, not deducting a blank for the impurities and reagents:

[Weights in milligrams.]

	Amount of KCl used.	Number of cc of impuri- ties used.	K_2PtCl_6 recovered from impu- rities, reagents, and KCl.	K_2PtCl_6 in reagents and impu- rities.	Per cent KCl re- covered from all sources.
I. KCl and regular impurities	375.1	15	1, 212.5	9.9	99.23
	375.1	15	1, 215.8	11.2	99.50
	375.1	15	1, 213.2	99.29
II. Same as I, except that 1 cc of a sat- urated solution of $MgCl_2$ was added	375.8	13.25	1, 213.2	7.5	99.10
after precipitation with NH_4OH and	375.8	13.25	1, 213.7	7.5	99.15
$(NH_4)_2C_2O_4$.	375.8	13.25	1, 213.6	7.5	99.14
III. Same as I, except that a small amount of Fe_2Cl_6 was added to the im- purities.	375.1	15	1, 215.6	99.49
	375.1	15	1, 216.2	99.54
	375.1	15	1, 215.8	99.50
IV. Same as III, except that $MgCl_2$ was employed as in II.	375.3	15	1, 216.5	99.51
	375.3	15	1, 214.2	99.32
	375.3	15	1, 214.1	99.31

¹Jour. Am. Chem. Soc., Vol. XVII, No. 6, p. 453.

²Vol. XVII, No. 1, p. 46.

Owing to the absence of blanks in III and IV and to the less quantity of reagents and impurities in II, there seemed to be no object in attempting to reduce the results to a common basis. Under IV it will be seen that one result is higher than the lowest in III, so that the data here reported appear to be too few to admit of any definite conclusions at this time. Notwithstanding these considerations, it has been deemed wise to report the results for the purpose of comparison with data which may possibly be recorded later by other workers.

(C) *On the result of repeated washing with alcohol and 60 cc of the ammonium chlorid wash employed in the Lindo-Gladding method.*

Winton reports the following:

Per cent KCl at end of first washing with ammonium chlorid and alcohol, 99.56; at the end of the second washing, 99.45; and at the end of the third washing, 99.34, or a loss of 0.11 per cent from each washing. This result is in accord with the lower results by the Lindo-Gladding method by direct evaporation—where no impurities were present in the double salt.

(D) *In further support of previous results showing that double decomposition between ammonium chlorid and potassium chlorplatinate actually results.*

Winton reports the following:

A quantity of K_2PtCl_6 which had been used for at least a year for saturating successive portions of ammonium chlorid solution was washed thoroughly with alcohol, to remove ammonium chlorid and to remove suspended matters, dissolved in water, filtered, and evaporated to dryness. A portion of the material thus obtained gave by distillation with caustic soda 1.08 per cent of nitrogen, equivalent to 17.10 per cent of $(NH_4)_2PtCl_6$.

Your reporter having noticed that occasional results during the last two years have been higher by the Lindo-Gladding than by the alternate method in case of direct evaporation, raised the question if, in cases where the ammonium chlorid is left continually standing in contact with the double salt (as is the custom of some workers), a sufficient amount of KCl might not accumulate in the solution so that it would be precipitated from the wash clinging to the crucible and filter upon the addition of strong alcohol, and thus cause an appreciable error.

W. G. Brown, of the Department of Agriculture, having at disposal a solution of the ammonium chlorid wash, prepared as above indicated, "evaporated 100 cc, and heated in a water oven. After volatilization of the ammonium salt at as low a temperature as possible, the residue was moistened with a solution of pure oxalic acid and reignited. Water was added and the solution filtered into a weighed platinum dish. Upon drying at 100° the residue weighed 0.0196 gram. It was then heated to low redness and again weighed. It now weighed 0.0178 gram. The colorless residue dissolved easily in water and gave the potassium spectrum." These results, while obtained with a somewhat different object, furnish further evidence of double decomposition. Owing to the small amount of wash clinging to the crucibles, it is not probable that any considerable amount of error from this cause can arise, and whatever it may be it would tend to counteract that due to the double decomposition during washing, and to solubility of the double salt in 80 per cent alcohol.

(E) *On some sources of error in potash determination.*

One analyst reports that by the Lindo-Gladding method, provided the heating subsequent to the addition of sulfuric acid is not conducted slowly, errors amounting to 6 per cent may arise in determinations involving 0.5 gram of pure KCl each. Winton also mentions losses by spattering unless special care is taken. Similar losses are also said to occur in expelling ammonium salts in the alternate method. C. G. Hopkins advocates the use of the factor based upon the atomic weight of platinum as 194.8. Veitch calls attention to the fact that one method prescribes the use of 80 per cent and the other of ordinary alcohol, in washing; and suggests that uniformity is desirable. Where potassium is determined in presence of sodium it has been recommended to break up the crystals of the double salt with a glass rod so that the sodium salt would be more readily dissolved. Hartwell finds, however, that

care must be taken that the precipitates are not pulverized by the process, or great difficulty will be experienced in filtering, owing to the passage of the fine material through Gooch crucibles and ordinary or acid washed filter papers in amounts sufficient to cause a serious error. The material which thus passes is so fine as to readily escape notice, and only becomes observable upon the intervention of a second filter, upon the surface of which it becomes visible.

The PRESIDENT. The regular order of business following the report is the reception of any papers bearing upon this subject. Are there any papers to be presented upon the subject of potash determination? If there are no formal papers, the discussion of this report is in order.

Mr. WINTON. Mr. President, I have no paper to present, but I wish to call attention to a couple of papers which have some bearing on this subject. I have found in a series of investigations results which have been published elsewhere, that make not only a difference in the appearance of the chlorplatinat precipitate, but also a considerable difference in the results. These experiments relate to the manner of precipitating the potassium chlorplatinat. The only difference in manipulation is in the degree of concentration of the solutions. It would not seem probable that this difference in manipulation would make any difference in the results, but nevertheless such is the case. The results in two cases differ by some 0.6 per cent potassium chlorid, or 0.4 potassium oxid. When these two preparations (showing the samples) were dried at 130° and 160° , we got a great reduction in weight. Ordinarily, with the precipitate obtained from a strong solution, it takes a long time at a high temperature to reach constant weight, while in the case of dilute solutions it dries in two hours. The explanation of these results is found in the fact that the crystals formed quickly in concentrated solutions inclose particles of the mother liquor, which are held with great tenacity on drying. The precipitations, therefore, should be made in a dilute solution, and this slowly evaporated to secure crystals free of mother liquor.

The PRESIDENT. The formal recommendations of the reporter on potash are now in order.

Mr. WHEELER. I think there is only one recommendation that the reporters desire to make, and that is that the alcohol be made to read 80 per cent instead of strong alcohol in one, and 80 per cent in the other. The recommendation is that all alcohol washing be made with 80 per cent alcohol.

Mr. PAYNE. It might be advisable to make a suggestion that in section 2 of our potash determination the muriate of potash be dissolved and made up to a volume of half a liter.

Mr. H. B. McDONNELL. I would recommend that the temperature for drying be made higher— 130° instead of 100° .

Mr. WINTON. I think the recommendation would be a good one provided it is necessary to heat at 130° .

Mr. FREAR. When Mr. Winton's report first appeared, I was much gratified, and it seems to me it is of considerable importance in con-

nection with this matter. While, of course, the evaporation of a diluted solution occupies more time, it seems that the point at which we should make the precipitation is in dilute solution rather than to make it at a later time. If, by taking a little longer time in evaporation, we can secure crystals which do not contain these impurities, it seems to me that that is the method we should follow rather than to increase the temperature of drying. My judgment would be in favor of securing such conditions as always to have the purest possible crystals.

The CHAIRMAN. The report on food and feeding stuffs is in order.

REPORT ON THE INVESTIGATION OF METHODS FOR ANALYZING CATTLE FOODS.

By H. J. PATTERSON.

The work outlined upon cattle foods for the past year was based upon the recommendations which were presented and adopted by the association at its last meeting, and consisted in directing our efforts solely to the investigation of methods for the determination of *crude fiber* and the *direct* determination of some of the *nitrogen-free extractive* matters. Samples, with instructions for this work, were ready for distribution by the middle of November. During the year, upon request for the same, twenty-one sets of samples have been sent to American chemists, and ten sets prepared for foreign workers. From these, reports have been received from six American chemists and two foreign chemists. The most of these reports have been only upon a portion of the work outlined. Eleven chemists report no work done; one reports results lost by fire, and the balance have not been heard from.

The following were the lines of work proposed and the methods suggested:

INVESTIGATION OF METHODS FOR CRUDE FIBER DETERMINATIONS.

- (1) Official method, proceedings Eleventh A. O. A. C. meeting, 1894.
- (2) Take 2 grams of the substance, place it in a strong flask, add 200 cc boiling $1\frac{1}{2}$ per cent H_2SO_4 ; cork the flask tightly, and heat in a water bath at 90° for three-fourths of an hour, with frequent shaking; filter, wash, and bring back into the flask with 200 cc boiling $1\frac{1}{2}$ per cent $NaOH$; cork the flask tightly, and heat in the water bath for forty-five minutes at 90° ; filter, wash, and proceed as in the official method.
- (3) Proceed as in (2), except using one-half per cent solutions and heating for two hours.
- (4) Proceed as in (3), using HCl instead of H_2SO_4 .
- (5) Test the method of V. Stein, Experiment Station Record, V, page 613—use 200 cc of the solutions and digest for five hours.
- (6) Try the method of Cross and Bevan for the determination of pure cellulose. (Jour. Chem. Soc. (London) Trans. 1893, p. 837.)

NOTE.—Test for the presence of starch in all cases. Use samples Nos. 2 and 3.

METHODS FOR THE DIRECT DETERMINATION OF NITROGEN-FREE EXTRACT CONSTITUENTS.

- (1) *Dextrose*.—Weigh out 3 grams of the substance into a beaker, add 50 cc H_2O and allow to stand for one hour, filter¹ into a graduated flask, and make up to 250 cc. Determine dextrose after Allihn's method (Eleventh A. O. A. C. report, Bull. 43, p. 356).
- (2) *Sucrose*.—Use 50 cc of filtrate from (1) and follow method (d), Bulletin 43, page 360.

¹ If the solution is hard to filter, add 2 cc alumina cream, prepared as described in Bulletin 43, page 359.

(3) *Starch*.—(a) Convert starch in residue from (1) into dextrose after the method of Sachsse (Chem. Centralbl. 1877, p. 732; Jour. Anal. Chem., II, 153) and determine dextrose as in (1). (b) Convert starch in residue from (1) into dextrose after the method of Märker (Chem. Zeit., IX, 319; Ztsch. Anal. Chem., 24, 617; Jour. Anal. Chem., II, 156) and determine dextrose as in (1). (c) Convert starch into dextrose after method of Stone (description herewith). (d) Use method (5) in W. E. Stone's paper (Eleventh A. O. A. C. report, Bull. 43, p. 165).

(4) *Pentosans*.—Use the method described herewith.

SACHSSE'S METHOD FOR THE DETERMINATION OF STARCH.

(Chem. Centralbl. 1877, p. 732; Jour. Anal. Chem., II, 153.)

Heat the residue from (1) (3 grams of the substance freed from the water soluble matter) on a boiling water bath for three hours, with 200 cc water and 20 cc of 25 per cent HCl (sp. gr. 1.125), in a flask provided with a reflux condenser; cool, and neutralize with Na_2CO_3 , and then make up to 250 cc and determine dextrose by Allihn's method.

The weight of dextrose multiplied by 0.9 gives the weight of starch, considering the formula to be $\text{C}_6\text{H}_{10}\text{O}_5$.

MÄRCKER'S METHOD FOR THE DETERMINATION OF STARCH.

(Chem. Zeit., IX, 319; Ztsch. Anal. Chem., 24, 617.)

Heat the residue from (1) (3 grams of the substance with water soluble matter extracted) with 50 cc H_2O to 90° , and after cooling to 65° , mix with 5 cc cold malt extract (50 grams malt extracted with 1,000 cc H_2O). Digest for thirty minutes at 60 – 65° ; then add 10 cc of 1 per cent tartaric acid solution, and heat the mixture under a pressure of 3 to 4 atmospheres for thirty minutes,¹ cool to 65° , add 5 cc malt extract, and maintain at this temperature for thirty minutes, then filter and wash. To the filtrate add 15 cc of 25 per cent hydrochloric acid, make up to about 200 cc and heat on a boiling water bath for two and one-half hours; neutralize with sodium carbonate and estimate the dextrose by Allihn's method. Calculate the dextrose to starch.

W. E. STONE'S METHOD FOR THE DETERMINATION OF STARCH.

Free the substance from fats and soluble carbohydrates by extraction with ether and water successively. Heat 3 to 5 grams to boiling for ten minutes, with 50 cc of water. Cool to 60° to 62° , add 10 cc malt infusion² and maintain at this temperature until the solution no longer gives the starch reaction with iodine. Filter and wash thoroughly. To the filtrate, which should have a volume of about 150 cc, add 15 cc of HCl (sp. gr. 1.125), and heat on a water bath for two and one-half hours. Neutralize with Na_2CO_3 and make up to 250 cc; determine dextrose by the method of Allihn and calculate the dextrose thus estimated to starch.

DETERMINATION OF PENTOSANS.

Place 2 to 5 grams of the material in a distilling flask with 100 cc HCl of 1.06 sp. gr. The mixture is then distilled and the distillate collected in a graduated receiver. For each 10 cc lost by distillation run in 10 cc HCl (sp. gr. 1.06) from a graduated stoppered funnel. Continue the distillation as long as the distillate shows the furfural reaction with anilin acetate. Neutralize the distillate with Na_2CO_3 . If the

¹Temperature 135° to 140° .

²Prepare the malt infusion by digesting 5 grams of fresh finely ground malt with 50 cc H_2O for 3 hours at the ordinary laboratory temperature, filter, wash, and make up to 100 cc; determine the amount of dextrose in 10 cc of this infusion by treating the same as in the determination of starch.

volume is less than 400 cc, add 10.2 grams NaCl for each 50 cc less than that volume, and dilute with H_2O to 400 cc. Add 10 cc of a 12 per cent solution of phenylhydrazin in glacial acetic acid and let stand, with frequent stirring, for twenty-four hours. Filter and wash with 100 cc of cold water. Dissolve off the filter with a small quantity of warm alcohol, collecting in a small tared flask. Evaporate the alcohol and dry at 60° . The weight of the phenylfurfurolydrazone multiplied by 0.744 gives the weight of the pentosans originally present. (References: Jour. Anal. Chem., V, 421, and VII, 68; Am. Chem. Jour., 16, 218.)

CRUDE FIBER INVESTIGATION.

For the work on crude fiber two samples were sent out—No. 2, a sample of corn meal, and No. 3 tobacco leaves.

There were but six reports received upon the work outlined above; some of the reports were upon only a portion of the work, and other reports were obtained by the use of methods different from those outlined.

The following table gives the results as obtained by the different chemists:

Crude fiber determinations.

Analyst.	Sample No. 2.				
	1 1.25 per cent H_2SO_4 and NaOH boiled for 30 minutes.	2 1.25 per cent H_2SO_4 and NaOH heated for 45 minutes at 90° .	3 0.5 per cent H_2SO_4 and NaOH heated for 2 hours at 90° .	4 0.5 per cent HCl and NaOH heated for 2 hours at 90° .	5 V. Stein's method.
United States Department of Agriculture, W. H. Krug.....	<i>Per cent.</i> 2.57	<i>Per cent.</i> 3.66	<i>Per cent.</i> 3.64	<i>Per cent.</i> 3.62	<i>Per cent.</i> 6.22
Illinois Station, C. G. Hopkins.....	2.61	4.59
Maryland Station, H. J. Patterson.....	2.95	4.39	4.33	4.30
Canada Station, F. T. Shutt.....	2.62
Germany, Dr. Fassbender.....	3.74
Norway, F. H. Wermskiold.....	3.01

Analyst.	Sample No. 3.				
	1 1.25 per cent H_2SO_4 and NaOH boiled for 30 minutes.	2 1.25 per cent H_2SO_4 and NaOH heated for 45 minutes at 90° .	3 0.5 per cent H_2SO_4 and NaOH heated for 2 hours at 90° .	4 0.5 per cent HCl and NaOH heated for 2 hours at 90° .	5 V. Stein's method.
United States Department of Agriculture, W. H. Krug.....	<i>Per cent.</i> 8.37	<i>Per cent.</i> 11.19	<i>Per cent.</i> 10.60	<i>Per cent.</i> 10.43	<i>Per cent.</i>
Illinois Station, C. G. Hopkins.....	8.68	10.77
Maryland Station, H. J. Patterson.....	9.10	10.32	10.87	10.20
Canada Station, F. T. Shutt.....	10.01
Germany, Dr. Fassbender.....	10.05
Norway, F. H. Wermskiold.....	9.91

In addition to the above, Mr. F. T. Shutt, chemist of the Canada Experiment Station, sent the results of the determination of crude fiber by the method used in his laboratory. The method, briefly, is as follows:

Two grams are taken, dried in steam bath for three hours, then digested for five hours in cold gasoline, dried, and boiled one-half hour with 250 cc of 1.25 per cent H_2SO_4 (approximately). This boiling is done in a round-bottomed evaporating dish which possesses a blue line showing the containing mark for 250 cc. Water is added from a wash bottle during the boiling to keep the fluid up to this mark. The fiber is now filtered and washed free from acid by hot water, using a suction apparatus.

It is then boiled with 250 cc of 1.25 per cent (approximately) NaOH, filtered and washed free from alkali, finally washed with alcohol, dried in a steam bath, weighed, ignited, and the ash deducted.

The results with this method were, with sample No. 2, 2.42 per cent, and sample No. 3, 9.61 per cent.

The following results, in addition to the above, were reported from the Illinois Station, by C. G. Hopkins:

	Sample No. 2.	Sample No. 3.
	<i>Per cent.</i>	<i>Per cent.</i>
Official method	2.61	8.68
1.25 per cent H_2SO_4 and NaOH digested for forty-five minutes at 90°	4.59	10.77
1.25 per cent H_2SO_4 and NaOH digested for two hours at temperature of boiling H_2O	3.48	8.88
1.25 per cent H_2SO_4 and NaOH digested for two hours at temperature of boiling, but previously extracted with ether for sixteen hours.....	2.63	7.80

Mr. Hopkins wishes to call the attention of the association to the use of Schleicher and Schuell's hardened filters No. 575, size 15 or $18\frac{1}{2}$ cm., for the first filtration in crude fiber.

He states that they stand the suction well, filter rapidly and thoroughly, and that the substance is easily removed from the filter by washing into the soda solution. He also states that the results obtained by the use of these filters are higher than when linen is used, but gave no figures. For the second filtration Mr. Hopkins uses a Caldwell-Gooch crucible with 1 mm. perforations and protecting the asbestos felt by means of platinum disk, as recommended by Puchner (Jour. Am. Chem. Soc., XV, 710).

It will be seen from the above table that the results with the official methods are the most uniform and satisfactory. Therefore I would recommend that the present official method be allowed to stand; but I believe that we should continue our search for a method using weaker solutions and conducting the heating in some manner so as to obviate the variations in temperature and amount of liquid at different stages of the operation which may obtain with the present method.

NITROGEN-FREE EXTRACT.

For the work outlined above on the direct determination of some of the nitrogen-free extractive matters, two samples were sent out—No. 1 consisting of a mixture of 2,000 grams of starch, 500 grams of cane sugar, 200 grams of gum tragacanth, and 100 grams of dextrose; No. 2 was a finely ground sweet corn. Both of these samples proved very difficult to filter—No. 1 no doubt due to the gum tragacanth, and No. 2 probably to some starchy matter. From the fact that it took a long time to filter No. 1 and was almost impossible to get a clear filtrate from No. 2, it would hardly be expected that the results would be very uniform.

Reports upon the determination of dextrose.

	Sample No. 1.	Sample No. 2.
	<i>Per cent.</i>	<i>Per cent.</i>
Arizona Station, R. H. Forbes.....	3.73	5.05
New Hampshire Station, F. W. Morse.....	3.84	4.68
Massachusetts Station, J. B. Lindsey	2.34	6.37
Maryland Station, H. J. Patterson	3.03	5.09
Average	3.24	5.30
Difference between highest and lowest.....	1.50	1.69
Greatest variation from average.....	.90	1.07

Reports upon the determination of sucrose.

	Sample No. 1.	Sample No. 2.
	<i>Per cent.</i>	<i>Per cent.</i>
Arizona Station, R. H. Forbes	15.54	3.36
New Hampshire Station, F. W. Morse	18.96	4.32
Massachusetts Station, J. B. Lindsey	11.68	¹ 13.61
Maryland Station, H. J. Patterson	19.70	3.40
Average	16.47	3.69
Difference between highest and lowest	8.02	.96
Greatest variation from average	4.79	.63

¹ Excluded from averages.*Reports upon the determination of starch.*

	Sample No. 1.	Sample No. 2.
<i>Method of Sachsse.</i>	<i>Per cent.</i>	<i>Per cent.</i>
Arizona Station, R. H. Forbes	64.17	40.56
New Hampshire Station, F. W. Morse	57.83	¹ 64.80
Massachusetts Station, J. B. Lindsey	62.69	36.57
Maryland Station, H. J. Patterson	57.33	31.95
Average	60.50	36.36
Difference between highest and lowest	6.84	8.61
Greatest variation from average	3.67	4.41
<i>Method of Mürcker.</i>		
Massachusetts Station, J. B. Lindsey		36.98
Maryland Station, H. J. Patterson	55.00	26.21

¹ Excluded from averages.*Reports upon the determination of pentosans.*

	Sample No. 1.	Sample No. 2.
	<i>Per cent.</i>	<i>Per cent.</i>
United States Department of Agriculture, W. H. Krug	10.26	9.08
Arizona Station, R. H. Forbes	3.92	5.99
Massachusetts Station, J. B. Lindsey	4.77	4.97
Norway, F. H. Wermskiöld	4.52	8.24
Average	5.87	7.07
Difference between highest and lowest	6.34	4.11
Greatest variation from average	4.39	2.01

The results as given in the above tables are very far from satisfactory—first, from the fact that they represent the work of so few analysts; and second, from the fact of the wide variation between the results of the various analysts. Yet, bad as these results may appear on first inspection, they are no worse than much of our work upon ether extract and crude fiber when this association first took up that work, and not much worse than some results on these determinations that are handed in at this time. If we review the initiatory work of the association upon butter, crude fiber, and reverted phosphoric acid, we will see that there was no more warrant for the adop-

tion of provisional methods than above results would justify; consequently, I think we may feel encouraged with what little has been accomplished.

I wish to call the attention of the association to the following methods, and suggest them as probably worthy of investigation: "The quick estimation of starch," by P. L. Hibbard (Jour. Am. Chem. Soc., vol. 17, p. 64); and "The quantitative estimation of starch," by J. Krieger (Jour. Soc. Chem. Ind., 1895, p. 199).

I wish to acknowledge at this time and place the very full report upon the samples for 1894 sent in by Dr. J. Sebelien, of Norway. This report came to hand too late for last year's proceedings, and the results can not be incorporated so as to be compared with this year's work.

RECOMMENDATIONS.

(1) That the methods for analysis of cattle foods be allowed to stand as they are at present.

(2) To continue the work on nitrogen-free extract from the fact that some experiment stations are now making investigations which call for methods for the direct determination of nitrogen-free extract matters, so that what work may be carried on in this line may be compared.

That the following additions be adopted as provisional methods to be used in the analysis of grains and by-product cattle foods:

- (a) The methods given above for the determination of *dextrose* and *sucrose*;
- (b) The method of Sachsse for the determination of starch in potatoes;
- (c) The method of Tollens and Flint as modified by Krug for the determination of pentosans;

and that the results be stated as follows:

Water.	
Asb.	
Crude protein.	
Crude fiber.	
Nitrogen-free extract	{ Dextrose.
	{ Sucrose.
	{ Starch.
	{ Pentosans.
	{ Undetermined.
Crude fat.	

Mr. LINDSEY. I should like to make a few remarks in relation to this subject, for I think it is one in which little progress has been made relative to bringing about improved methods, for the good reason that it is a most difficult line of work. We are dealing with physiological substances. They are so intricate that it is a difficult problem to separate them into their several constituents. In the matter of crude fiber it seems to me it is time to call a halt or else go at it in a different way. So far as I understand the matter, those who have dealt with it in the past have attempted to find a method that would give us reliable results—that is, they recognized crude fiber as a single substance, while of course all know that it is not, crude fiber being simply a combination of substances—a part of a group of substances. We have used the official method because we have had no other better one. We all know crude fiber is a combination of three things—cellulose, lignose, and pentosans. They are recognized as substances that can be dissolved and converted into sugar by the action of diluted acid. They are as a rule classified with that group. I believe crude fiber will be recognized as a group for a

long time to come, for on that is based all our knowledge of food stuffs. At the same time, I think we can find a method of determining pure cellulose. I think the line should be drawn there. We should attempt to find a method for determining the cellulose itself.

I should like a committee especially interested in this work to be appointed to confer together and to suggest the line of work which should be carried out. I think we ought to progress more in this than we have.

The PRESIDENT. Without formally appointing a committee, we will ask those particularly interested on this matter to confer with each other and with the reporter sometime during the meeting. I shall be glad to be present when this takes place.

At 12.30 the convention adjourned until 1.30 p. m.

THURSDAY—AFTERNOON SESSION.

The PRESIDENT. The first thing to consider will be the report of the committee in regard to the proposed changes in the methods for determining potash. The report of the committee was adopted, and the proposed changes were incorporated in the official methods of analysis. (See Bulletin 46, pp. 21 et seq.)

Mr. McDONNELL. There has been, I think, an unauthorized change made in the temperature at which this precipitate is dried. It should be 130° instead of 100°.

Mr. LINDSEY. The committee, without making any formal recommendation, would like to suggest the investigation of the question of change of factor for calculating potash and potassium chlorid, from the weight of chlorplatinat obtained.

The PRESIDENT. The report on soils and ash is now in order.

REPORT ON SOILS AND ASH.

By A. M. PETER and ARTHUR GOSS.

In accordance with the action of the association last year, your reporters have given to the study of the solubility of the phosphoric acid and potash of soils in dilute acid solutions a prominent part in this year's work. In addition to this, it was decided to continue the study of the sulfuric-acid method as applied to the determination of phosphoric acid and potash in soils, and to test further the present association method for these substances. The work upon ash was confined to the association method.

The ash used was that of corn fodder or stover, and was prepared in exactly the same way as sample No. 4 of last year.¹

The soils were selected as follows:

Sample No. 1.—From plot 5, acre P, Kentucky Experiment Station farm; collected November 22, 1894, by taking up, with a tool made for the purpose, cylindrical cores of soil to the depth of 6 inches from 60 different places at regular intervals over the whole extent of the plot (one-tenth acre). In this way about 70 pounds of soil were obtained, and this, after thorough mixing with a spade, was sifted through a one-eighth-inch mesh sieve and thoroughly air-dried; it was then mixed again and stored in a box from which the samples sent out were taken. These samples were not bottled, but simply wrapped in paper.

¹ U. S. Department of Agriculture, Div. Chem. Bull. 43, p. 29.)

Acre P of the Kentucky Station has been planted with corn for seven years in succession previous to the taking of this sample, in an experiment with commercial fertilizers, in which each plot received the same fertilizer every year. The plot in question (No. 5) received available phosphoric acid and nitrogen at the rate of 57 and 26 pounds per acre, respectively, each year, in the form of acid phosphate and nitrate of soda. The yield from this plot in 1894, calculated to the acre, was: ear corn, 1,078 pounds; fodder, 2,030 pounds.

Sample No. 2.—From plot 5 of the field of the Rhode Island Experiment Station at Kingston, used for experiments with fertilizers on corn from 1890 to 1894, in which year miscellaneous crops were grown, collected by H. J. Wheeler in a manner similar to that described under Sample No. 1, but taking the soil from the south two-thirds of the plot and from about twelve places only. The soil was a sandy loam, containing much vegetable matter, giving it a dark chocolate color. The rock fragments sifted out were granitic in character. This plot had received in fertilizers each year, beginning with 1890, about 25 pounds of nitrogen and 76 pounds of potash per acre, in the form of nitrate of soda and muriate of potash.

Sample No. 3.—From acre P, plot 6, Kentucky Station; collected and prepared in the same way and at the same time as No. 1. This plot had received each year 80 pounds of potash per acre and about 26 pounds of nitrogen in the form of muriate and nitrate. The yield from this plot in 1894, calculated to the acre, was 2,457 pounds ear corn and 3,130 pounds fodder.

Sample No. 4.—From plot 2 of the Kingston, R. I., field; collected by H. J. Wheeler in the same way as No. 2. This plot had received each year about 50 pounds of available phosphoric acid per acre in the form of dissolved bone black.

CHARACTER OF THE SOILS.

The series of field experiments conducted upon the Kentucky soil by this station during a period of seven years, indicates that this soil is well supplied with available phosphoric acid, but does not afford available potash enough to support an average crop of corn, potatoes, or tobacco. It responds readily to potash manures, but not to phosphates. The Rhode Island soil is the reverse of this in regard to phosphoric acid, responding to phosphates in a marked manner, as shown by the experiments during five years at that station. In regard to available potash, the supply seems to be better, perhaps, than that of the Kentucky soil, though the yields seem to be better where both phosphates and potash are applied, showing that the supply of available potash is not yet sufficient for the demands of the crop.

Upon these facts the selection of these soils for this year's work was based, but upon a more careful consideration of the subject your reporters have become convinced that, on account of the acid character of the Rhode Island soil and its large proportion of vegetable matter, the selection of this soil was not well made. At any rate, these properties should be borne in mind when considering the results herein reported. In selecting the Kingston soil it was intended to obtain a soil deficient in available P_2O_5 , just as the Kentucky soil was selected on account of its deficiency in available K_2O ; but the highly vegetable character of the former was at first overlooked, and it was not realized, until after the selection was made, that this circumstance might vitiate a comparison of the Rhode Island and Kentucky soils, and render the results exceptional in character. Nevertheless it is believed that the results obtained are of value and have brought out some points which would not have been so evident had the soils not been so different in character.

DIRECTIONS FOR WORK ON THE SOIL AND ASH SAMPLES.

The directions sent out with the samples were substantially as follows, the references being to the "Proceedings of the Eleventh Annual Convention of the Association of Official Agricultural Chemists," published as Bulletin 43, Division of Chemistry, United States Department of Agriculture:

The solvent used in (2) is that proposed by Bernard Dyer¹, but experiments made

¹ Jour. Chem. Soc., London, Vol. LXV, 1894, p. 115; see also Wiley's Agricultural Analysis, Vol. I, p. 344.

here seem to indicate that the time of digestion he adopts—seven days—is much too long.

Besides the work indicated, it is desirable to know the action of a given solvent for different lengths of time, for different amounts and concentrations, and upon other soils of well-known character, especially such as have been proved by field experiments to be deficient in available P_2O_5 while possessing sufficient available K_2O to produce a crop, or vice versa. It would also be desirable to have comparative results on these samples by other methods, with the use of other solvents, such as dilute HNO_3 (Schloesing), dilute HCl , ammonium citrate, etc. Results of any such additional work will be gratefully received and properly credited in the report to the association.

The ash.—Analyze by the association method, page 390. The sample is ready for analysis without further preparation.

The soils.—Weigh each sample and prepare it (p. 386) by sifting upon a one-half mm. mesh sieve, rubbing the coarse part in a mortar with a rubber pestle (a rubber stopper answers) until the gravel is as completely separated as possible from the fine earth. Weigh the gravel and report its amount per cent of the original soil; mix the fine earth well and preserve it in a tightly stoppered bottle, from which the portions for analysis are to be weighed out.

If a sieve with circular openings is not at hand, use the ordinary sieve with meshes as nearly as possible one-half mm. in diameter. The ordinary 40-mesh is about right.

1. Determine moisture in each sample as described on page 386, and note that results are to be stated as percents of the soil dried in the water oven. To avoid calculation, it is therefore suggested to weigh out quantities of the fine earth corresponding to the required number of grams of dried soil.

2. Put 200 grams of each sample into bottles or flasks of at least $1\frac{1}{2}$ liters capacity and pour on each exactly 1 liter of a solution of citric acid containing 10 grams of the crystallized acid to the liter; cork and shake well, and allow to digest at the temperature of the laboratory, or about 20° , with frequent thorough shaking, for exactly five hours. If convenient, an automatic shaking device may be used, provided all the bottles can be shaken at once, and its use should be mentioned in reporting the results. At the end of the digestion, shake the contents of the bottles well and pour quickly upon a large dry ribbed filter, collecting the filtrate in a dry flask. The filter paper should be at least 12 inches in diameter, better 14 inches, and of quality equal to S. and S. 597, or heavier. Shaking up the soil before pouring it on the filter helps to produce a clear filtrate. If the first 10 or 20 cc come through muddy, they may be rejected or returned to the unfiltered portion, but it is best to let the filtration go on as rapidly as possible. Evaporate 625 cc of the filtrate, corresponding to 125 grams of soil, in a porcelain dish to a small volume, transfer to a platinum dish of about 100 cc capacity, bring to dryness on the water bath, and burn off all the organic matter at a very low heat, barely redness. After the residue has been charred it is very light and easy to burn at a temperature at which there is little danger of loss of potash salts. After burning, transfer the dry residue to a low beaker of about 200 cc capacity, cover, and add about 30 cc strong HCl , using the HCl to rinse the last traces of the residue from the dish; heat on the water bath until effervescence has ceased, remove the cover, and evaporate to dryness, finishing the drying, if necessary, on the sand or air bath at a higher temperature. The residue is to be taken up with 4 or 5 cc HCl and a little water and digested on the water bath until the iron compounds have been dissolved; it is then transferred to a 250 cc measuring flask, cooled, made up to volume, mixed by shaking, and filtered through a dry filter into a dry flask.

(a) For P_2O_5 , measure 100 cc of this solution (= 50 grams soil) into a beaker, evaporate to about 50 cc, and determine as in (7), page 388. About 50 cc of the molybdcic solution will be required.

(b) For K_2O , 100 cc of the solution (= 50 grams soil) are diluted with about an equal volume of water and precipitated boiling hot with a slight excess of NH_4OH and enough ammonium oxalate to throw down the lime. The precipitate is filtered, using pressure and well washed with hot water. The filtrate and washings are evaporated to dryness, and the ammonium salts expelled by cautious ignition barely to redness in a porcelain or platinum dish. The residue is to be dissolved in a little warm water, and the K_2O determined in the filtrate as in the alternate method, page 350. Two cc of the usual $PtCl_4$ solution will be found to be about the proper quantity to add.

A blank experiment should be made with 625 cc of the citric acid solution and the same amounts of reagents are used, in order to correct for any P_2O_5 or K_2O contained in them.

3. Two hundred grams of each sample are to be digested in exactly the same way as in 2, substituting for citric acid a solution of 6.3 grams of oxalic acid to the liter, and determining P_2O_5 and K_2O in the resulting solution, as just described.

4. Two hundred grams of each sample are to be treated exactly as before, using a solution containing 20 grams of crystallized ammonium oxalate and 2.15 grams of

anhydrous acetic acid, C_2H_3O, OH , to the liter. This solution may be prepared by first making a solution of ammonium oxalate, containing 40 grams of the crystallized salt to the liter, and a dilute acetic acid containing 4.30 grams of C_2H_3O, OH to the liter, as determined by titration against standard KOH , or $NaOH$, and mixing together equal measures of these two.

5. Determine P_2O_5 and K_2O dissolved by HCl of 1.115 sp. gr. by digesting 10 grams, as directed on page 387, (1), and determining P_2O_5 as on page 388, (7).

For the K_2O , evaporate 100 cc of the HCl solution nearly to dryness to expel the excess of HCl ; take up with about 200 cc of water and precipitate boiling hot with a slight excess of NH_4OH , adding also enough ammonium oxalate to throw down the lime; filter, wash thoroughly with hot water, evaporate to dryness, and expel the NH_4 salts by cautious heating, and determine the K_2O in the residue as in the alternate method, beginning with the corresponding stage of the process.

If time permit, please report also the per cent of insoluble matter obtained in the HCl digestion, page 387, (1).

6. Determine P_2O_5 by the Goss method, page 58. Also note that the molybdate solution used must be full strength. An old solution in which the greater portion of the molybdic acid has crystallized out will not answer. It is safest to use a recently prepared solution.

7. The following method for potash has been worked out by one of us (A. G.), and is here submitted for trial:

First, test all the reagents used by running a blank determination, as under the working directions.

Weigh out 5 grams of soil and transfer to a round-bottom hard-glass digesting flask marked to hold 250 cc; add 0.7 gram yellow oxide of mercury, 5 cc concentrated sulfuric acid, and 10 cc concentrated nitric acid; cover mouth of flask with a watch glass and digest for one hour over a flame just sufficient to keep the contents of the flask boiling gently, without expelling the acid too rapidly. If the boiling has proceeded too rapidly and the acid becomes too low before the end of the hour, 10 cc more of nitric acid may be added. (If the digestion is to be continued several hours, a sand bath will be necessary, as the contents begin to bump badly after two or three hours boiling.) When the digestion is finished, fasten a clamp to neck of flask just above bulb and heat over lamp until the nitric acid is all expelled and the white fumes of sulfuric acid appear. During this heating the contents of the flask should be kept constantly rotating to prevent spattering. The heating should not be discontinued too soon, as it is desirable to secure the action of the sulfuric acid alone for a few minutes. After the nitric acid is all expelled, cool, fill flask about one-half full of water, boil for a few minutes to break up the cake, cool, and add ammonia in slight excess (indicated by the formation of a permanent precipitate); add 20 cc of saturated ammonium oxalate solution and sufficient yellow ammonium sulfid solution to impart a yellow color to the liquid in the flask (10 or 15 cc of a well-saturated solution will be sufficient). Fill flask nearly to mark with water, wire in a rubber stopper, and digest in a water bath at from 70° to 80° for thirty minutes, cool, make up to volume, filter through a dry paper, transfer 100 cc of the filtrate to a platinum dish, and evaporate to dryness over the water bath. A stirring rod should be placed in the dish and the cake of sulfur which forms over the surface broken up occasionally. When the ammonium salts begin to form a crust over the surface, vigorous stirring for a few minutes will cause them to crystallize out and allow the evaporation to be quickly completed. When the evaporation is finished, wipe off the stirring rod with a small piece of quantitative filter paper, which is to be dropped into the dish, transfer to an air bath at a temperature of 150° , and heat until perfectly dry, from one-half to one hour. Catch the dish with a pair of platinum-tipped tongs, which are supplied with a clamp to hold them closed; carefully ignite over an ordinary Bunsen burner until ammonium salts are expelled, and then over a blast lamp for a minute or two until the filter paper is entirely burned out and the dish has been red hot all over. Dissolve the potassium sulfate in water with the addition of 10 drops concentrated hydrochloric acid free from ammonium salts, by digesting over the water bath for fifteen minutes, filter into a platinum or porcelain dish, wash with hot water, add 2 cc of platinum solution, and evaporate to dryness; add 1 cc of water and 20 cc of 95 per cent alcohol; place the dish over water bath until the alcohol begins to boil; filter, wash thoroughly with 95 per cent alcohol, then with ammonium chlorid solution, and finally very thoroughly with alcohol. Good results can not be secured unless the washings, and especially those with alcohol, are very complete. Before beginning the second washing with alcohol it is well to wipe off the ammonium chlorid from the funnel above the paper. Transfer paper and precipitate to an air bath at 110° , dry for thirty minutes, place paper in funnel, and dissolve precipitate in water almost at boiling temperature, receive filtrate in a weighed platinum dish, evaporate to dryness, dry at 110° for thirty minutes, cool in a desiccator, and weigh.

Reagents.—The yellow ammonium sulfid solution is made by adding an excess of flowers of sulfur to a bottle of strong ammonia, and thoroughly saturating with H_2S , shaking at intervals. When no more sulfur will dissolve, stopper tightly and filter off as needed.

The other reagents not already described are the same as used in the Lindo-Gladding method, as described in the A. O. A. C. proceedings.

LEXINGTON, KY., *March 12, 1895.*

THE RESULTS.

Twenty-two sets of samples were sent out, and reports were received from fourteen chemists, the results being summarized in the following tables:

Tables I and III need no explanation. In Table II the percentages of P_2O_5 and K_2O obtained from each sample, calculated upon the fine earth dried in the water oven, are given in the columns headed with the numbers of the respective samples. In the last three columns in each division are given the differences between the percentages of P_2O_5 or K_2O , as the case may be, obtained in the samples indicated by the two numbers at the head of each of these columns. Thus, under phosphoric acid, we have, in fifth column, headed No. 1—No. 3, the difference between the percents of P_2O_5 obtained in soils Nos. 1 and 3, and, as soil No. 1 has received available P_2O_5 in the fertilizers applied to it for a number of years, and soil No. 3 has received none, this difference should represent the excess of P_2O_5 in No. 1 over that in No. 3, due to the combined effects of fertilization and cropping. The same thing is shown for the Rhode Island soil in the sixth column, headed No. 4—No. 2. In the seventh column, headed No. 3—No. 2, we have the difference between findings of P_2O_5 in the Kentucky and Rhode Island soils, respectively, where none has been applied in the fertilizer, and, inasmuch as the Kentucky soil is known to contain an abundance of P_2O_5 , mostly in available form, and the Rhode Island soil appears to be deficient in this constituent, this difference ought to be considerable, and ought to represent an amount which would be considered a liberal supply of phosphoric acid. As regards potash, the differences in the column headed No. 3—No. 1 should represent the accumulation of this constituent in soil No. 3 over that in soil No. 1, due to fertilization and cropping, and in this case it seems to be proved by the field experiments at the Kentucky Station that enough has accumulated to supply a very fair crop of corn on No. 3, while No. 1 will not produce an average one. The same thing is shown for the Rhode Island soil in the column headed No. 2—No. 4; and in the last column, headed No. 4—No. 1, is the difference between the amounts of K_2O in the Rhode Island and Kentucky soils, respectively, where no K_2O has been applied to either in the fertilizer. The methods of analysis employed are indicated at the left of the table.

TABLE I.—*Gravel, moisture, and insoluble residue.*

[Gravel is stated as per cent of the air-dried sample; moisture as per cent of the air-dried fine earth; insoluble residue as per cent of the dried fine earth.]

Soil.	L. M. Bloomfield, Ohio.	Arthur Goss, New Mexico.	F. W. Trapbagen, Montana.	Harry Snyder, Minnesota.	John Thompson, Minnesota.	W. G. Brown, U. S. Department of Agriculture.		C. C. Moore, U. S. Department of Agriculture.		Chas. Ryan, Colorado.	F. P. Veitch, Maryland.	F. T. Shutt, Ottawa, Canada.	C. B. Williams, North Carolina.		A. M. Peter, Kentucky.		Geo. S. Fraps (Student), North Carolina College of Agriculture.	R. F. Hare, New Mexico.
						First set of samples.	Second set of samples.	First set of samples.	Second set of samples.				First set of samples.	Second set of samples.	First set of samples.	Second set of samples.		
Soil No. 1:																		
Gravel.....	11.200	8.33	11.170	4.350			1.700	3.779		11.415		18.8	4.749	5.454	310.81	39.23		
Moisture.....	1.955	1.870	1.996	1.900			2.458		2.690	2.290		2.26	1.69		2.865	2.43		2.00
Residue insoluble in HCl.	83.610				81.990		282.13	80.335	80.80			82.19						
Soil No. 2:																		
Gravel.....	18.400	7.47	12.370	10.58			4.164	6.323		15.88	15.27		10.813	10.727	312.64		12.87	
Moisture.....	1.910	1.990	2.428	2.24			2.584		2.640	2.590	2.46		1.45		3.18		2.46	1.95
Residue insoluble in HCl.	84.290				83.42		384.16	84.545	83.655									
Soil No. 3:																		
Gravel.....	114.50	9.27	20.37	7.56			2.114	3.315		18.049			7.762	7.742	39.82	310.32		
Moisture.....	1.81	1.92	2.07	1.90			2.264		2.790	2.340			1.78		2.57	2.17		1.98
Residue insoluble in HCl.	83.01				82.12		381.75	79.815	80.665									
Soil No. 4:																		
Gravel.....	14.94	11.88	7.72	5.91			1.993	3.029		9.247			6.267	6.685	37.430			
Moisture.....	1.98	2.06	2.262	1.76			2.382		2.660	2.380			1.53		2.440			2.00
Residue insoluble in HCl.	83.71				83.13		384.03	83.770	83.745									

¹ Used a 30-mesh sieve.² Digested several hours with HCl, 1.21 sp. gr., in beaker and evaporated on the residue, repeating this operation a second time.³ Washed and dried before weighing.

Acetic acid = 1 per cent citric. ¹		2 hrs.	do	.0014	.0004	.0017	.0009	—	.0003	.0005	.0013	.0013	.0031	.0043	.0018	.0030	.0079	.0005
Citric-acid solution, 10 grams per liter.	Hand shaken, following reporter's directions.	8 days	do	.0021	.0019	.0019	.0019	.0002	.0002	.0002	.0014	.0014	.0030	.0046	.0021	.0030	.0079	.0005
		2 hrs.	do	.0169	.0107	.0154	.0125	.0015	.0018	.0047	.0040	.0111	.0073	.0021	.0033	.0090	.0019	
		5 hrs.		.0345	.0210	.0260	.0210	.0085	.0000	.0050								
				.0306	.0156	.0256	.0192	.0050	.0036	.0106								
2 per cent citric acid.	Hand shaken			.0210	.0150	.0120	.0200	.0090	.0050	.0036	.0037	.0100	.0062	.0034	.0025	.0046	.0003	
				.0190	.0250	.0210	.0160	.0020	.0030	.0040	.0030	.0060	.0040	.0016	.0010	.0044	.0014	
				.0193	.0119	.0161	.0116	.0032	.0003	.0042	.0024	.0115	.0028	.0016	.0004	.0099	.0008	
				.0237	.0183	.0249	.0180	.0012	.0003	.0066	.0032	.0130	.0071	.0060	.0019	.0070	.0008	
				.0220								.0185						
				.0266							.0043							
				.0481	.0111	.0248	.0157	.0233	.0046	.0137	.0416	.0220	.0172	.0315				
				.0285	.0134	.0245	.0158	.0040	.0024	.0111								
				.0298	.0227	.0290	.0187	.0008	.0040	.0063	.0050	.0143	.0260	.0059		.0084	.0009	
				.0350	.0200	.0310	.0190	.0040	.0010	.0110								
				.0268	.0178	.0235	.0175	.0033	.0003	.0057	.0039	.0122	.0050	.0037	.0011	.0085	.0002	
				.0188		.0165		.0023			.0039		.0069		.0030			
2 per cent citric acid.	Hand shaken	6 hrs.		.0410	.0280	.0380	.0240	.0030	.0040	.0100	.0040	.0140	.0070	.0050	.0030	.0090	.0010	
		10 hrs.																
		24 hrs.		.0312		.0304		.0008			.0053		.0072		.0019			
		3 days		.0518	.0482	.0487	.0549	.0031	.0067	.0005	.0031	.0138	.0058	.0022	.0027	.0116	.0009	
		5 days		.0555	.0522	.0555	.0629	.0000	.0107	.0033	.0022	.0132	.0070	.0015	.0048	.0117	.0007	
		7 days		.0634	.0629	.0603	.0686	.0031	.0037	.0026	.0025	.0120	.0056	.0015	.0031	.0105	.0010	
		7 days		.0487		.0480		.0007			.0052		.0082		.0030			
		24 hrs.		.0510	.0400	.0510	.0440	.0000	.0040	.0110								

¹Acidity equivalent to a 1 per cent solution of crystallized citric acid, as determined with normal KOH and phenolphthalein.

TABLE III.—*Ash sample.*

[Figures in italics are not included in the averages.]

	L.M.Bloom- field, Ohio. ¹	Chas. Ryan, Colorado. ¹	Chas. Ryan, Colorado. ²	B.C. Keiser, Kentucky. ¹	Average.
Soluble SiO ₂	15.14	20.938	20.327	15.09
Insoluble SiO ₂ (sand).....	45.48	37.278	37.803	45.77
Total SiO ₂	60.62	58.216	58.130	60.86	59.46
K ₂ O.....	5.88	5.841	5.332	5.42	5.63
Na ₂ O.....	.90	1.776	1.305	.71	1.18
CaO.....	11.38	12.125	11.258	11.14	11.48
MgO.....	7.93	6.862	7.093	7.65	7.38
Mn ₂ O ₄26	Trace.11	.19
Fe ₂ O ₃	1.40	3.780	{ 3.780 }	1.96	1.68
Al ₂ O ₃	3.91	.91
P ₂ O ₅	7.57	7.560	7.327	7.02	7.52
SO ₃	1.01	1.030	1.017	.95	1.01
CO ₂83	1.19	1.19	1.01	1.01
Cl.....	1.17	1.13	1.13	1.10	1.13
Moisture.....	.1414
Carbon.....	1.18	.860	.703	1.15	.97
Total.....	100.27	100.370	98.265	100.59	99.69

¹ Official method.² Colorado Station method.³ Separated from the Fe₂O₃ by the tartaric acid and ammonium sulfid method.

REMARKS AND EXTRACTS FROM REPORTS OF ANALYSTS.

L. M. Bloomfield.—Time did not permit making blanks to test chemicals. The gravel was separated with a 30-mesh sieve, after repeated pestling with a rubber-tipped pestle. Moisture is the mean of two determinations made at different times. Citric acid soluble P₂O₅, is the mean of two independent determinations. Solutions prepared by shaking by hand at intervals of five to ten minutes. Had difficulty in the ash analysis when Fe₂Cl₆ was not used.

F. W. Traphagen.—The methods of the circular were followed, except in the phosphomolybdate precipitation, which was made in shorter time. The filtrate showed no sign of the presence of P₂O₅. Thinks that ten hours' digestion with HCl is too long, and suggests that five hours' digestion be investigated next year.

W. G. Brown and C. C. Moore.—The first set of samples being insufficient, a second lot of the same material was furnished these chemists. The differences in the amounts of gravel separated will be noted, as also those between the percentages of insoluble residue, which latter are means of closely agreeing duplicates. The percentages of moisture are "the lowest obtained after drying in some cases for thirty-one hours, it being found that, whether the samples were dried in covered or uncovered dishes, the weights varied from weighing to weighing—sometimes increasing, sometimes diminishing." The five hour digestions were made according to the reporter's directions, the flasks being shaken about every fifteen minutes. In those for three, five, and seven days the solutions were shaken every fifteen minutes during seven hours each day, resting during the remaining time. The mechanical shaking was at the rate of 50 to 60 times per minute. These digestions were made at about 20°. An experiment made at 30° gave with 1 per cent citric acid on soil No. 1, 0.0281 per cent P₂O₅ and 0.0025 per cent K₂O; with the acetic acid and ammonium oxalate solution on soil No. 4, 0.0281 per cent P₂O₅ and 0.0036 per cent K₂O, indicating a marked increase of solubility, especially of the P₂O₅, with increase of temperature. It is quite prob-

able that this fact may account for some of the discrepancies appearing between the results of different analysts, and particular attention is here called to it.

Charles Ryan.—The ammonium oxalate and acetic acid solution filtered badly and the solvent was in contact with the soil for a much longer time than the other solvents which filtered very freely. P_2O_5 in No. 1 by this solvent was not satisfactory, and is probably too high. The method of ash analysis practiced at the Colorado Station is briefly described by Dr. Headden, as follows:

To 50 cc of my solution, equivalent to about 1 gram ash, I add Fe_2Cl_6 in excess; then Na_2CO_3 and $NaC_2H_3O_2$ in sufficient quantity to assure the conversion of my bases into acetates, and evaporate to dryness. The precipitate contains the whole of the P_2O_5 , and no lime. The filtrate is always clear and small in volume, and the Mn_2O_4 precipitates readily. I find the reprecipitation of the calcium oxalate to be almost imperative, provided ammonium oxalate enough is added to convert both the Ca and Mg into oxalates. The determinations with which I have the greatest difficulty are the SO_3 , CaO, and MgO.

Dr. Headden states that, if the solution is not made too nearly neutral before evaporating, there is no danger of Ca, Mg, or Mn going down with the iron precipitate. The reporter has not had time to test the method, but if it works as well as Dr. Headden claims, it certainly has very marked advantages, avoiding, as it does, the need for accurate neutralization and the handling of bulky precipitates and solutions, and deserves further trial. Dr. Headden also calls attention to the plus error in SO_3 when precipitated as $BaSO_4$ in presence of alkali salts, etc., and to the loss of S and Cl in the preparation of an ash, rendering it desirable to have a method for the determination of these substances without burning.

C. B. Williams.—Determined P_2O_5 both gravimetrically and volumetrically, the figures in Table II under the latter head being means of several closely agreeing results, obtained by a method which forms the subject of a paper read before this association. Briefly, the method consists in precipitating the phosphomolybdate in the usual way, after which it is filtered and washed and "dissolved back into the same beaker with $2\frac{1}{2}$ per cent ammonia; run in nitric acid until the precipitate just begins to form; add 10 grams of ammonium nitrate, and heat to 65° in water bath and nitric acid added, with vigorous stirring till slightly acid. At the end of five minutes added 2 cc molybdic solution; let stand eight minutes, filtered, washed, and titrated according to Kilgore's method." Mr. Williams's duplicates by this method were very close, but when reprecipitation was not resorted to they presented considerable variation. He reports 2.25 per cent P_2O_5 in the gravel of soil No. 1.

DISCUSSION OF RESULTS.

Gravel.—From Table I it appears at once that the present method of separating the gravel from the fine earth is highly unsatisfactory. Your reporter separated about 10 per cent of clean, washed iron gravel from soils 1 and 3, in which other observers reported from 1.7 to 20.37 per cent. It is evident that an uncertain amount of the gravel is pulverized in the process of separation. The remedy which suggests itself is to avoid so much pulverization in the determination of available P_2O_5 and K_2O , etc., where large quantities of soil are taken, by the use of a coarser sieve; but for those determinations such as the general analysis or total P_2O_5 or K_2O , where comparatively small quantities of soil are taken, to pulverize the gravel until it passes the one-half mm. sieve, and mix it with the fine sample, thus insuring uniformity of material. Your reporters therefore recommend that the method of preparation of the sample for analysis be modified to include the following: (1) The sample to be sifted first through a sieve with circular openings 2 mm. in diameter. A portion of this is to be made to pass a sieve with circular openings one-half mm. diameter, grinding if necessary. The coarser soil is to be used in determinations, for which 100 grams or more of soil is weighed out; the finer in those for which smaller portions are taken.

Total acid-soluble P_2O_5 .—As appeared last year, a greater uniformity obtains in the results by the Goss method than in those by the official method. This is shown more clearly in the following table:

TABLE IV.—*Goss's method for P_2O_5 compared with the official method.*

	Per cent P_2O_5 by Goss's method.				Per cent P_2O_5 by official method.			
	Average 5 chem- ists.	Highest.	Lowest.	Differ- ence, as per cent of the average.	Average 4 chem- ists. ¹	Highest.	Lowest.	Differ- ence, as per cent of the average.
Sample No. 1.....	.462	.490	.442	10.4	.451	.510	.324	41.2
Sample No. 2.....	.251	.287	.219	27.1	.172	.268	.117	87.8
Sample No. 3.....	.450	.470	.429	9.1	.396	.462	.409	13.4
Sample No. 4.....	.262	.320	.214	40.5	.193	.267	.095	89.1

¹ Findings by 5 chemists are included in No. 1.

It is also apparent that ten hours' digestion in HCl sp. gr. 1.115 does not extract from soils 2 and 4 all the P_2O_5 that is capable of solution in strong acids, and it is probable that the same thing will hold for vegetable soils generally. In the opinion of your reporters the present method for P_2O_5 by HCl digestion is unsatisfactory, and should be replaced by one which will insure in all cases the complete extraction of all the P_2O_5 that is capable of solution in strong acids. This should eventually be supplemented by a method for determining the solubility of this P_2O_5 in weaker solvents. As a step in this direction, your reporter would recommend (2) that the Goss method for P_2O_5 be adopted as an optional method.

Available P_2O_5 and K_2O .—To intelligently discuss the results obtained by the action of weak solvents, we must bear in mind the character of the soils as determined by field experiments. This has already been briefly given, and from it we would expect that any method capable of giving results in agreement with those of field experiments should bring out the following relations:

(1) The amount of available P_2O_5 shown should be large in soils 1 and 3 and small in 2 and 4, and the difference should represent an amount sufficient to supply a crop for many years. Besides this, soil 1 should contain distinctly more than soil 3, and 4 distinctly more than 2.

(2) The amount of available K_2O shown should be small in soils 1 and 3, and probably somewhat larger in 2 and 4, though this last point is not as clearly brought out by the field results as could be desired. Besides this, soil 3 should contain distinctly more than soil 1, and 2 distinctly more than 4.

As these soils, taken to the depth sampled, weigh approximately 1,000,000 pounds per acre, the figures in Table II may be made to roughly represent pounds per acre by moving the decimal point four places to the right. For convenience, the averages by the three principal solvents tested, expressed in this way, are brought together in the following table, together with some individual results that seem to be of special significance in this connection.

TABLE V.—*Available P₂O₅ and K₂O in pounds per acre.*

Number of soil	Phosphoric acid.				Potash.			
	1	2	3	4	1	2	3	4
Fertilizers applied contained	PN	KN	KN	P	PN	KN	KN	P
Pounds of P ₂ O ₅ or K ₂ O applied per acre in seven years less that removed in the crop in same time.	219	1—267	1—134	297
Average per year	31	42
Citric acid, five hours' digestion (average)	268	178	235	175	39	122	50	37
Acetic acid and ammonium oxalate, five hours' digestion (average)	733	331	661	286	60	142	113	54
Oxalic acid, 6.3 grams per liter, five hours' digestion (average)	562	153	575	180	60	158	74	77
Oxalic acid, equivalent to 1 per cent citric, two hours' digestion (Peter and Keiser)	1, 135	319	1, 062	356	40	117	87	29
Oxalic acid, 1 per cent, five hours' digestion (Jaffa)	1, 100	200	1, 040	250
Acid potassium oxalate, equivalent to 1 per cent citric, two hours' digestion (P. and K.)	1, 067	133	976	189
Acetic acid, equivalent to 1 per cent citric, two hours' digestion (P. and K.)	14	4	17	9	13	97	43	18

¹ Removed in the crop during seven years.

It is readily seen that the relations looked for are brought out in a more or less perfect manner by each of the solvents tried, but it appears that five hours' digestion with oxalic acid, 6.3 grams to the liter, while it brings them out better than the 1 per cent citric acid, does not do so as well as a stronger solution of oxalic acid. The indications are that more advantageous conditions and perhaps better solvents may be found than those tried this year. For this reason your reporters desire simply to report progress in this direction without recommending any method for available P₂O₅ and K₂O in soils.

Total nitrogen.—With many soils it is almost impossible to boil 14 grams with 20 cc H₂SO₄, and the amount of nitrogen present is often such that it is not necessary that as much as 14 grams be used. Your reporters therefore recommend (3) that in the method for total nitrogen, page 389 (13), instead of "14 grams of soil" read "7 to 14 grams of soil."

Ash analysis.—The same difficulty seems to exist in the separation of soluble silica and sand as last year, for which we have no remedy to suggest. It is very apparent also that the amount of acid prescribed for re-solution of the residue after evaporation to dryness is insufficient, and that it is imperative to remove all P₂O₅ from the solution before the separation of Mn, Ca, and Mg. We therefore recommend: (4) on page 390, under the heading "Analysis of the ash," fourth line of the paragraph, for "with 2 or 3 cc HCl" read "with 5 or 10 cc HCl;" and, (5) on page 391 (2), after "50 to 100 cc of Solution A," insert the words "after the addition of enough FeCl₃ solution to combine with all the P₂O₅ present."

Your reporters desire to express their thanks to the chemists who took part in the soil and ash work for their generous cooperation.

RECOMMENDATIONS OF THE REPORTERS ON SOIL AND ASH.

(1) The soil to be sifted first through a sieve with circular openings 2 mm. in diameter, a portion of this to be made to pass a sieve with circular openings one-half mm. diameter, grinding if necessary. The coarser soil is to be used in all determinations for which 100 grams or more is weighed out, the finer in those for which smaller portions are taken. (Such are the general analysis, total P₂O₅ and K₂O, etc.)

(2) That the Goss method for P_2O_5 be adopted as an optional method.

(3) In method for nitrogen, page 389 (13), instead of "14 grams of soil" read "7 to 14 grams of soil."¹

(4) On page 390, under the heading "Analysis of the ash," fourth line of the paragraph, for "with 2 or 3 cc HCl" read "with 5 or 10 cc HCl."

(5) On page 391 (2) insert, after "50 to 100 cc of Solution A," the words "after the addition of enough Fe_2Cl_6 solution to combine with all the P_2O_5 present."

The recommendations were considered by the committee on recommendations of reporters and reported back as follows:

(1) Same as reporters' No. 2.

(2) Same as reporters' No. 3, with the addition of the words "except in case of muck or peat soils."

(3) Same as reporters' No. 4.

(4) Same as reporters' No. 5.

The committee also reported, in regard to the suggestions of Professor Whitney, substantially that, while they recognized the importance of physical methods in the examination of soils, they did not consider it necessary to recommend the appointment of a reporter upon this subject, especially as there is now a division of the U. S. Department of Agriculture devoted to it.

The recommendations as finally adopted by the association read as follows:

(1) That the Goss method for P_2O_5 be adopted as an optional method.

(2) Total nitrogen is determined by the Kjeldahl method, modified to include nitrates, as described by the committee on nitrogen.

(3) On page 390, under the heading "Analysis of the ash," fourth line of the paragraph, for "with 2 or 3 cc HCl," read "with 5 or 10 cc HCl."

(4) On page 391 (2), after "50 to 100 cc of Solution A," insert the words "after the addition of enough Fe_2Cl_6 solution to combine with all the P_2O_5 present."

MECHANICAL ANALYSES.

Prof. Milton Whitney kindly consented to have mechanical analyses of the soils made in the laboratory of the Division of Agricultural Soils, and a set of the reporters' samples was furnished him. The following are the results—Nos. 153 and 279 being the Rhode Island soils (reporters' Nos. 2 and 4), and Nos. 130 and 277 being the Kentucky soils (reporters' Nos. 1 and 3):

No.	Analyst.	Moisture in air-dry sample.	Organic matter.	Gravel, 2-1 mm.	Coarse sand, 1-0.5 mm.	Medium sand, 0.5-0.25 mm.	Fine sand, 0.25-0.1 mm.	Very fine sand, 0.1-0.05 mm.	Silt, 0.05-0.01 mm.	Fine silt, 0.01-0.005 mm.	Clay, 0.005-0.0001 mm.
		<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>
153	J. P. Alexander	1.72	8.92	4.37	5.23	9.53	8.49	26.79	25.43	6.34	5.55
	S. Key	2.15	7.62	2.71	4.74	9.52	8.62	27.18	29.10	4.03	4.37
	Do	1.33	9.27	.55	2.67	8.21	8.01	33.32	27.35	3.57	5.80
	Average	1.73	8.60	2.54	4.21	9.90	8.37	29.10	27.29	4.65	5.34
279	J. P. Alexander	1.71	8.56	1.82	3.21	6.28	5.13	27.53	36.54	*4.32	4.94
	S. Key	2.16	8.96	.23	1.54	5.32	4.41	39.76	29.13	3.68	3.95
	Do	2.36	7.43	1.24	2.99	5.65	5.31	35.31	30.60	4.29	3.97
	Average	2.08	8.32	1.10	2.58	5.75	4.95	34.20	32.09	4.10	4.29

* By difference.

¹ NOTE.—It was understood that the rest of paragraph (13), beginning with "When the digestion is completed," etc., shall remain the same as now, the new reading taking the place of the first sentence only.—A. M. P.

Mechanical analyses of the soils—Continued.

No.	Analyst.	Moisture in air-dry sample.	Organic matter.	Gravel, 2-1 mm.	Coarse sand, 1-0.5 mm.	Medium sand, 0.5-0.25 mm.	Fine sand, 0.25-0.1 mm.	Very fine sand, 0.1-0.05 mm.	Silt, 0.05-0.01 mm.	Fine silt, 0.01-0.005 mm.	Clay, 0.005-0.0001 mm.
130	J. P. Alexander	Per ct. 1.94	Per ct. 7.28	Per ct. 3.36	Per ct. 3.46	Per ct. 2.45	Per ct. 1.42	Per ct. 4.01	Per ct. 35.50	Per ct. 20.39	Per ct. 21.45
	S. Key	2.59	6.08	2.31	4.32	2.73	1.12	4.53	49.75	11.72	15.44
	Do	2.30	6.31	1.40	3.41	2.62	1.01	5.85	49.39	10.64	16.60
	Average	2.28	6.46	2.36	3.73	2.60	1.22	4.81	44.88	14.25	17.83
277	J. P. Alexander	1.90	7.14	2.46	2.94	2.48	1.41	5.23	40.16	16.28	21.00
	S. Key	2.53	6.32	1.33	3.13	2.81	1.27	5.51	50.48	12.19	14.08
	Do	2.16	6.78	.93	3.18	3.05	1.25	7.15	48.54	10.04	17.47
	Average	2.20	6.75	1.57	3.08	2.78	1.31	5.96	46.39	12.84	17.52
	Average of 153 and 279 (reporters' 2 and 4) ..	1.90	8.46	1.82	3.40	7.82	6.66	31.65	29.69	4.38	4.81
	Average of 130 and 277 (reporters' 1 and 3) ..	2.24	6.60	1.96	3.40	2.69	1.26	5.28	45.63	13.54	17.67

The analyses were made by the Osborne beaker method, slightly modified as to some of the details.

The results are practically identical for 153 and 279 (Rhode Island soils), and for 130 and 277 (Kentucky soils), which was to be expected, considering the origin of these samples, as already explained.

In commenting upon this report Professor Whitney remarks:

From this analysis I would have no hesitation in assigning to samples 153 and 279 a very different agricultural value from samples 130 and 277. The former have the same texture as our early truck soils, while the latter have the same texture as our corn and wheat lands, being in fact rather light for profitable wheat production.

The PRESIDENT. You have the report of the committee on soils and ash; are there any papers to be presented on this subject?

Mr. WHEELER. I have a short paper I would like to present.

ON THE NECESSITY OF TESTS FOR ACIDITY ON UPLAND OR NATURALLY WELL-DRAINED SOILS.

By H. J. WHEELER.

In 1890, in experiments with ammonium sulfate upon the Experiment Station farm at Kingston, R. I., it was found, when applied at the rate of 120, 240, and 360 pounds per acre. and in connection with muriate of potash and superphosphate, that injurious results followed, increasing generally in proportion with the amounts applied. The soil is a sandy loam underlaid by yellow loam and then alternating layers of sand and gravel, furnishing good natural drainage. The natural water level is from 15 to 18 feet below the surface, and the land is in no sense what would be termed heavy or wet. At Hope Valley, R. I., on sandy loam located on a hilltop, the results with ammonium sulfate under like conditions were good in 1890, fair in 1891, and in 1892 positively injurious. The soils in both localities, when stirred to a thick paste with water, impart to blue litmus paper a marked acid reaction which persists upon drying. An application of air-slacked lime fully corrected the condition and enabled the plants to derive their full beneficial effect from the ammonium salt, thus harmonizing with contemporaneous results secured by Paul Wagner and Dorsch, wherein they showed that marl increased the effectiveness of ammonium salts more than of

sodium nitrate in experiments with summer rape grown in peat (Torf). These results led to a study of the effect of acid soil upon the growth of various plants, and to tests of soil from Rhode Island, Massachusetts, Connecticut, and other States. Many soils were tested in localities where beets, spinach, onions, lettuce, and clover could not be grown with any measure of success, and where it was impossible to secure a good stand of certain kinds of grass. In all such cases marked acid reactions were obtained, though, owing to the lack of a suitable method for determining relative soil acidity, fully satisfactory comparisons of the soils could not be made. Tests with air-slacked lime in connection with beets at Westerly, R. I., though not completed, show a decided benefit under similar conditions, as has also an experiment on oats on a farm at West Kingston. It will thus be seen that positive data have been secured in three locations, two of which are at points from 15 to 20 miles remote from the Experiment Station farm. It should be stated here that tests for protosulfate of iron have been made on several occasions, which have given in every case negative results. Aqueous extracts from the soil give but a faint acid reaction, and have been found to contain salts of iron which show no iron reaction with ordinary reagents until after evaporation, ignition, and subsequent solution. These data show that protosulfate of iron is not the cause of the acid reaction, nor accountable for the injurious action of this soil upon the growth of certain plants, but rather that the acid reaction is probably due to extremely insoluble organic acids or acid salts. That such a condition should exist may seem at first thought surprising, but when we consider that the soil is derived from granite containing orthoclase instead of oligoclase, and mica instead of hornblende, it will be seen, particularly where the soils are composed chiefly of granitic drift containing much silica, that the amounts of bases liberated in the natural processes of decomposition are small compared with the amount of organic acids continually produced by the humification of decaying plants, and furthermore, under such conditions, the natural acidity must tend to delay nitrification, and to the conservation of humus within the soil. In a soil derived from rock containing an abundance of calcium carbonate such conditions are inconceivable. On theoretical grounds, then, having recognized the existence of acidity in such soils, and sometimes to such an extent as to seriously interfere with nitrification and with the growth of certain plants, even when supplied with nitrates, it must be apparent that a determination of the lime by the use of hydrochloric acid as a solvent can furnish no evidence of their productiveness even when the physical conditions are perfect and an abundant supply of all the essential elements is present. That such is actually the fact is shown by the continued ill effect for three years of ammonium sulfate when used in connection with calcium sulfate, and of its effectiveness when a like amount of calcium oxid has been employed in the form of air-slacked lime. It is furthermore shown in a striking way by experiments at the experiment station this season upon beets, where the use of calcium oxid in the form of land plaster, while of decided benefit to the crop, is far inferior to a like amount in the form of air-slacked lime.

In pot experiments with beets, where 900 pounds of sodium carbonate per acre has been used for two successive years, the results have been better than where air-slacked lime was used, in quantities amounting last year to $2\frac{1}{2}$ tons and this year to one-half ton per acre additional, and in the yield where magnesium hydroxid was employed in quantities representing the same basic action as the sodium carbonate, the results have been but little inferior to those with the air-slacked lime. It might perhaps be argued that this action of the sodium carbonate and magnesium hydroxid finds its explanation in the liberation of lime, yet this does not, in view of the experiments heretofore cited, seem probable except to a limited extent. In further support of the idea that acidity is the point with which we have chiefly to deal, and that the action of calcium carbonate, magnesium hydroxid, and sodium carbonate is attributable in a large measure to their neutralizing function, it should be stated that the results from the use of calcium carbonate and sodium carbonate have been

excellent with lettuce and spinach as well as with beets, and that most of these plants otherwise succumb to the acid conditions before developing their second leaves, and this occurs at whatever season of the year and largely regardless of soil conditions as concerns moisture. It may, however, be said that the injurious action is intensified in dry periods, possibly owing to the fact of greater intimacy of contact of the roots with the soil particles or to other causes. That there is not sufficient time to enable young beet, spinach, and lettuce plants to develop to the extent of perfecting a second pair of leaves is not possible in view of the fact that lime enough is present for the profitable production of many rye and Indian corn crops in succession, and this seems further impossible in view of the fact that a few of the beet plants which succeed in withstanding the conditions at the outstart, though never growing luxuriantly, yet produce roots of considerable size.

These statements seem sufficient to substantiate the position taken, and also to show that the soil conditions described are not confined to the limits of our Experiment Station farm, but that they exist at other points in the State, and perhaps elsewhere, in varying degrees of intensity. That such a condition of this class of soils has not heretofore been recognized in this country is not surprising, in view of the fact that the degree of acidity is perhaps never so great as to destroy all of the plants, even of those kinds which are most susceptible to acid conditions, and the fact that many die has probably been attributed to lack of vitality of the seed employed and to attacks of insects and fungi. Again, Indian corn, rye, several of the grasses, French turnips, potatoes, and several other plants, thrive nearly as well or better before liming than after, provided considerable lime is used and the crop immediately succeeds the liming. Barnyard manure and wood ashes are much used in our section, though in insufficient quantities to maintain fertility, and yet sufficient in amount to ameliorate somewhat the acid condition. Considering, therefore, the kinds of plants grown and this latter factor, there is less need for surprise at the previous nonrecognition of the acidity. On the other hand, where plants have failed, defective physical soil conditions or some other plausible theory has always suggested itself; as an example of which, we were told that clover would not succeed in our section owing to winterkilling. Notwithstanding this, however, by the aid of lime magnificent crops have been grown, and careful observation has shown that without lime the plants died, as a rule, before winter—a fact which the farmers failed to observe.

A visitor at our Station in 1894, who had viewed the experiments in the above-mentioned lines and who was familiar with experimental observations made upon the growth of garden vegetables in another State, asserted that there, no matter how well certain plants were supplied with potash, phosphoric acid, and nitrogen in form of chemicals, they failed to make a satisfactory growth, and that those plants were the very ones which in our experiments have been found to be most injured by our soil conditions. It has been most interesting to learn that subsequent trials of lime upon this land have been followed by the most gratifying results in connection particularly with wheat, clover, and timothy, all of which have been found to succeed poorly on our acid soil. That this soil is acid appears possible, though no opportunity for testing it has thus far been afforded.

If such conditions are found to exist to considerable extent among the exhausted lands of sections of New England and perhaps of other States, then the farmer, or the experiment station for him, is in position, by a simple, quick, and inexpensive test, to prescribe for the first needs of the soil, whereby it can be put in condition to produce profitable return for the money invested in the three so-called essential elements, particularly when those plants are grown which are not fully successful on acid soils. In the work by Galloway, in which the growth of lettuce in a Boston market garden soil was superior to that in a granitic soil from another place, the possibility suggests itself, in view of the great susceptibility of this plant to injury by acidity, that the previous barnyard manure treatment on the one hand and the

possible acidity of the soil on the other may have had their bearing upon the results, as well as the physical constitution of the soil to which the observed differences were wholly attributed. It is hoped that experimenters elsewhere, particularly in sections where limestone does not prevail and where the natural rocks are not of a basic nature, will make observations and experiments in the same line, for wherever such conditions prevail their recognition has a more important bearing and must be more far-reaching than a mere local observation that lime benefited certain plants.

Mr. WHEELER. I have also papers by Messrs. Harry Snyder and John Thompson which I desire to read to the association.

DETERMINATION OF THE TOTAL INSOLUBLE MATTER, PHOSPHORIC ACID, LIME, AND POTASH IN SOILS.

By HARRY SNYDER.

The complete analysis of a soil involves so much labor in the determination of elements which are of minor importance in agriculture that it seems best to concentrate the work so as to include only the more important constituents. In this method of procedure the phosphoric acid, lime, and potash precipitates are from the entire 5 or 10 grams of soil used, thus insuring larger quantities to work with, and at the same time each precipitation is also a preparation for the next operation, so that when the potash determination is reached it is not necessary to repeat the work of removing the ammonia and ammonium oxalate precipitates. The total insoluble matter is determined in the usual way by digestion in a soil flask.¹ The acid solution is precipitated with ammonia; the precipitated phosphoric acid, ferric oxid, and alumina are dissolved in dilute nitric acid, and the phosphoric acid determined by one of the official methods. The filtrate from the ammonia precipitate is concentrated, and the lime is precipitated with ammonium oxalate. The titration of the oxalate with permanganate will be found more rapid and equally as accurate as the gravimetric process. In dissolving the lime, in case there is a large quantity, much time will be gained by washing the precipitate into an Erlenmeyer flask with hot water, and not attempting to dissolve in dilute acid; 20 cc of H_2SO_4 are added, slowly, down the sides of the flask; the lime will then go into solution immediately without the use of any HCl . The H_2SO_4 raises the temperature of the solution to about the right degree for the titration.

Potash.—Up to this point all of the work has been preparatory to the potash determination. Inasmuch as the determination of the soil potash is by far the most difficult and is also one of the most important determinations, the details are given somewhat more fully.

The filtrate from the ammonium oxalate precipitate is evaporated to dryness and ignited in a platinum dish. The residue is dissolved in hot water, a few drops of ammonium oxalate added, and all insoluble matter removed by filtering. The filtrate is evaporated to dryness and ignited a second time. If the residue is completely soluble in hot water, which is rarely the case, the platinic chlorid (4 cc) solution is then added. If the residue is insoluble in hot water, the solution is filtered again and concentrated before adding the platinic chlorid. After the platinic chlorid is added, the solution is evaporated to a sirupy consistency, when the 95 per cent alcohol is added. Vigorous stirring of the solution materially hastens the precipitation of the double salt. The potassium chlorplatinate is collected on a small filter, washed first with alcohol until free from chlorin, then with 10 cc of a half-concentrated solution of ammonium chlorid saturated with potassium chlorplatinate to remove impurities, and finally with alcohol. In all of the filtrations the washings are continued until tests with silver nitrate give no reaction for chlorin.

¹Bul. 42, p. 386, U. S. Dept. of Agr. Div. Chem.

The precipitated double salt is dried to remove alcohol, the filters are then replaced in the funnels with the proper weighed platinum dishes under the funnels. Hot water is added to dissolve the double chlorid. There is, in the case of soils, a material amount of insoluble impurities left in the filters which would otherwise be weighed as potash. The solution is evaporated to dryness; the double salt is weighed after drying in an air bath at 120.

The separate removals of the ammonia and ammonium oxalate precipitates and the insoluble matters after ignition, as well as the final solution of the double salt, are all necessary in order to obtain a precipitate of potassium chlorplatinate free from impurities. The method as outlined has been followed in the analyses of the association soil samples, 1895:

	No. 1.	No. 2.	No. 3.	No. 4.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
Total insoluble.....	81.57	82.80	81.55	82.35
Phosphoric acid (P_2O_5).....	.48	.22	.40	.20
Lime (CaO)31	.18	.51	.21
Potash (K_2O).....	.25	.17	.26	.10

EFFECTS OF THE PRESENCE OF A FEW DROPS OF NITRIC ACID IN THE ACID DIGESTION OF SOILS.

By JOHN THOMPSON.

In the method of soil analysis as given by Dr. Hilgard the weighed quantity, etc., is treated with 8 to 10 times its bulk of hydrochloric acid of 1.115 sp. gr., and 2 to 3 drops of nitric acid, and digested for five days over the laboratory steam bath. In the method as outlined by Dr. Kedzie the nitric acid was omitted, but later it was added to the acid filtrate. In order to determine the effects of the presence or absence of these few drops of nitric acid, the present association samples were given both methods of treatment. Five grams of soil were digested with 50 cc HCl (1.115 sp. gr.). In Series II, 4 drops of nitric acid were added to the HCl. Hilgard advises 2 or 3 drops of HNO_3 with 2 or 2.5 grams of soil. The digestions of both series were continued for ten hours. The average differences, 0.22 per cent of less total insoluble matter, and 0.01 per cent more phosphoric acid, when the nitric acid is present, are very small, but it is to be noted they are always in favor of the increased solubility when the 4 drops of nitric acid are present.

	Soil No. 1.		Soil No. 2.		Soil No. 3.		Soil No. 4.	
	Series I, HCl.	Series II, HCl and HNO_3 .	Series I, HCl.	Series II, HCl and HNO_3 .	Series I, HCl.	Series II, HCl and HNO_3 .	Series I, HCl.	Series II, HCl and HNO_3 .
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
Total insoluble....	81.33	81.25	83.48	83.17	81.55	81.16	82.96	82.85
P_2O_559	.605	.205	.215	.515	.52	.205	.215

Averages: 0.22 per cent less insoluble matter with HNO_3 ; 0.01 per cent more P_2O_5 with HNO_3 .

Mr. Goss. I desire to present a paper on the determination of phosphoric acid and potash in soils.

CONCERNING THE DETERMINATION OF PHOSPHORIC ACID AND POTASH IN SOILS.

By ARTHUR GOSS.

I.—GENERAL CONSIDERATION.

Investigators in the subject of soil analysis seem to be pretty well agreed at present that at least two points should be aimed at in the analysis of soils—these are the plant food immediately available, and the reserve store which may be expected to become available in the future. Some knowledge of both these points seems to be necessary in order to draw correct conclusions in regard to the present and future ability of soils to produce plants. Neither alone may be of much value. It has been repeatedly demonstrated, for example, that the total amount of phosphoric acid or potash present in soils, or even the total amount of those substances soluble in strong acids, is often in no way proportional to their present plant producing powers, and it is not difficult to imagine a soil containing sufficient available phosphoric acid and potash for a few crops with insufficient total to insure any permanent fertility.

In regard to the proper solvents to use in the analysis of soils, if I may be permitted a word on that time-honored theme, I would say that for immediately available plant food it seems to me that a very weak solvent should be used, or at least the conditions of solution so regulated that only a very small amount of plant food should be dissolved.

It is a matter of very simple calculation to show that the amount of phosphoric acid and potash removed from an ordinary soil each year by plants is only a very small amount of the total present; hence, if we are to imitate plant action, it seems evident that a large amount of soil must be taken for analysis and a very small amount of plant food dissolved.

Furthermore, as the dividing line between the immediately available and the reserve store of plant food in a soil is not at all definitely drawn, it seems to me that any method for the estimation of available plant food in soils must necessarily be purely arbitrary. In the exhaustion of soils we do not secure maximum crops up to a certain point, after which no crops at all can be obtained; but, on the other hand, the exhaustion is a gradually decreasing process, and is never absolutely completed.

In regard to the solvent itself, it is a very difficult matter to determine what should be selected, owing to the decided difference in soils themselves and in the ability of different plants to secure food from soils. A great many different substances have been tried for this purpose, usually with more or less uncertainty as to interpretation of results secured. As acids exuded by the roots of plants undoubtedly play a more or less important part in securing food from the soil, the search for the proper solvent has been, very naturally, most often among the acids. As has already been noted, however, one objection to the use of a diluted acid is the fact that most soils contain magnesium and calcium carbonates, and other material which would to a greater or less extent neutralize a weak acid, and of course one could not expect the same solvent effect from the salts formed as from the acid itself. It has been suggested that this difficulty might be obviated by a preliminary determination of the basicity of the soil, and an excess of solvent added sufficient to neutralize the amount of base found. In the case of carbonates this might possibly be done with more or less certainty, and, I think, should be done if an acid solvent should be found most desirable. In the case of such basic material as iron oxid, however, the solution of which is only partial in weak acids, I do not see how it would be possible to make the correction for the dilution of the solvent with any degree of certainty. Any weak solvent would, however, be more or less open to the same objection.

Taking this fact alone into account, it would perhaps seem advisable to use a neutral solvent for the estimation of available phosphoric acid and potash, provided one could be found which would represent plant action. There are certain theoretical

considerations, however, a discussion of which lack of space will not permit me to enter into in this paper, that would seem to point to the use of an alkaline solvent for available phosphoric acid, and it is my intention to do some work along this line in the near future.

As the solubility of phosphoric acid and potash are so different, it may be found advisable to employ a different solvent for each.

Another point in connection with the determination of the availability of plant food in soils that seems to me to be of sufficient importance to warrant further work is the relative composition of plants grown on different soils. During the past season some very striking examples have come under my observation in regard to the ability of certain plants to take up an unusual amount of potash when that substance was present in the soil in very large amount. The important point at issue would, of course, be as to whether these plants grown in soils deficient in available potash would show a corresponding deficiency in the ash.

In regard to the reserve store of plant food in soils, it seems, for a number of reasons, to be of little importance in most cases to determine the total amount present. It can readily be seen, for example, that phosphoric acid or potash in the center of a quartz pebble would be totally unavailable, at least within present geological time; hence, the availability of phosphoric acid and potash may not be proportional to the total amount present.

As it seems to be true that mineral plant food in the soil can only enter the plant when in the form of solution, it would likewise seem to be true that the solubility of plant food in the soil should be a measure of its availability. This being the case, it would seem reasonable to suppose that of two soils which had been exhausted of their store of immediately available plant food the one yielding the greater amount to a solvent acting more rapidly than those at the command of plants would produce available plant food faster than one yielding a smaller quantity. To illustrate by an example, if two portions of some difficultly soluble material, one of double the quantity of the other, be treated for exactly the same length of time, which shall be insufficient to insure complete solution, with exactly the same amount of solvent, which shall be sufficient in quantity to insure an unsaturated solution, it will be found that more material has been dissolved in the case where the larger quantity of material was used. Moreover it would seem to be important as one part of the analysis to attack the soil with some strong solvent in order to gain some knowledge of the reserve store of plant food present. Such a treatment also becomes doubly important, as Hilgard has repeatedly pointed out, in the case of virgin soils where the amount of plant food soluble in strong solvents would naturally be expected to be to a greater or less extent proportional to their present fertility. It would therefore seem to be desirable to use one of the strong mineral acids as a measure of the solubility of the reserve store of plant food in soils.

As to the proper acid to use, as the matter at best can only be arbitrary, it seems to me that so far as interpretation of results is concerned it makes little difference whether we use hydrochloric, nitric, or sulfuric acid. In the case of phosphoric acid at least, I think that whichever acid is chosen should be allowed to act until solution is practically complete. It happens, fortunately, in the case of phosphoric acid, that the maximum solvent action of hydrochloric, nitric, and sulfuric acids usually seem to be about the same, so that for phosphoric acid, at least, it seems to me that we should be guided in the choice of a strong solvent very largely by the time necessary to reach the maximum solvent effect and by the ease and accuracy of subsequent manipulation. In regard to the time necessary to reach the maximum solvent effect, there can be no question as to the decided superiority of sulfuric acid, and as to ease and accuracy of subsequent work, with proper care, sulfuric acid is, in my opinion, quite as good as either hydrochloric or nitric. For these reasons I am very strongly in favor of sulfuric acid, aided by mercuric oxid, as the solvent for reserve phosphoric acid in soils.

The selection of the proper solvent for reserve potash is, in my opinion, a matter of more uncertainty, owing to the fact that the maximum solvent effect of different acids is quite liable to be decidedly different. So far as interpretation of results is concerned, it might be about as well to make the matter entirely arbitrary as to time of digestion, etc. If this should be done, hydrochloric acid, acting for a reasonable length of time, would, in my opinion, be the most desirable solvent.

If, on the other hand, it is thought desirable to work to the maximum solvent effect of one of the acids mentioned, there can be no doubt concerning the superiority of sulfuric acid, so far as the time necessary to reach that point is concerned. The use of sulfuric acid for this purpose is, however, unfortunately attended with some analytical difficulty, owing to the fact that in order to secure enough acid to successfully boil the necessary amount of soil the resulting solution contains so much of that acid or its salts that its expulsion becomes troublesome. By diluting the sulfuric acid, however, with two or three times its volume of concentrated nitric acid, this difficulty can largely be avoided. This mixture seems to reach the maximum solvent effect in a comparatively short time, and is withal about the most satisfactory solvent I have yet been able to find for that purpose. If, however, a ready means of expelling ammonium sulfate could be found, I would be in favor of using sulfuric acid alone.¹

The objection to the use of hydrochloric acid for this purpose is the great length of time necessary to secure maximum action, which, when the digestion is made at the boiling temperature, has been found to be five days, and in some cases even longer.

In this modern rush of affairs it seems to me that we can not afford to use analytical methods requiring such lengths of time if it is possible to avoid the same. It must be apparent to all who have done this class of work that unless the time required by most of the methods of soil analysis at present in use is very materially reduced, this subject must remain of minor importance.

It was thought, in this connection, that a tabulated statement of some results secured by myself and others in regard to the comparative action of sulfuric and hydrochloric acids in dissolving potash in soils might be of interest. The figures are given in Table I.

TABLE I.

Number of soil.	Kind of soil.	Where from.	Acid used.	Temperature at which digested.	Hours digested.	Per cent K ₂ O.
62.....	Sedimentary clay loam.	New Mexico Experiment Station.	5 cc H ₂ SO ₄ , 15 cc HNO ₃ .	(*)	1	1.37
62.....do.....do.....do.....	(*)	4	1.37
123.....	Clay.....	Knox County, Ind.....do.....	(*)	1	.57
123.....do.....do.....do.....	(*)	4	.52
133.....	Adobe.....	California.....do.....	(*)	1	1.20
133.....do.....do.....do.....	(*)	4	1.15
133.....do.....do.....	HCl.....	100°.....	120	†1.31
1895, A. O. A. C., 1..	Clay.....	Kentucky Experiment Station.	5 cc H ₂ SO ₄ , 15 cc HNO ₃ .	(*)	1	.53
Do.....do.....do.....	H ₂ SO ₄	100°.....	480	.56

* Boiling acids.

† Analyzed under the direction of E. W. Hilgard.

¹ The manipulation in the determination of potash in soils by the use of sulfuric, sulfuric and nitric, or any other strong acid method that I have tried, is somewhat difficult and requires considerable practice to secure satisfactory results. For this reason I do not believe we should be in a hurry to adopt any strong acid method for potash before the same has been thoroughly tried.

TABLE I—Continued.

Number of soil.	Kind of soil.	Where from.	Acid used.	Temperature at which digested.	Hours digested.	Per cent K ₂ O.
1894, A. O. A. C., 3..	Clay	Kentucky Experiment Station.	H ₂ SO ₄	(*)	1	.51
Do	do	do	HCl	100°	36	†.42
Do	do	do	HCl	100°	120	†.40
1894, A. O. A. C., 5..	do	Beard, Ky	H ₂ SO ₄	()	1	†.52
Do	do	do	HCl	100°	36	†.51
2304.....	do	Helena	H ₂ SO ₄	(*)	1	†.79
2304.....	do	do	HCl	100°	36	†.72
2306.....	do	do	H ₂ SO ₄	(*)	1	†.70
2306.....	do	do	HCl	100°	36	†.63
121.....	Clay	Beard, Ky	H ₂ SO ₄	(*)	1	.50
121.....	do	do	HCl	100°	36	.53
124.....	Clay loam....	Knox County, Ind...	H ₂ SO ₄	(*)	1	.55
124.....	do	do	HCl	100°	120	.45
99.....	Clay	do	H ₂ SO ₄	(*)	1	.45
99.....	do	do	HCl	100°	120	.41

* Boiling acids.

† Analyzed by A. M. Peter.

‡ Average from 1894 A. O. A. C. soil work.

By referring to the figures in Table I, the first thing apparent is the considerable variation in results, making general conclusions more or less uncertain. This would naturally be expected, however, in the case of a determination where the proportional amount of substance dissolved varies in different cases and is often only a small portion of the total amount present.

It would seem, however, that one hour's boiling with sulfuric or sulfuric and nitric acids usually removes about as much potash as longer treatment with the same solvent, and that this amount is usually somewhat similar to that secured by the usual long-time digestion with hydrochloric acid. There are doubtless exceptional cases, however, in which one hour's boiling with sulfuric acid would not entirely reach the maximum solvent effect of that acid; but I believe such cases are not very common.

II.—CONCERNING THE MAXIMUM SOLVENT EFFECT OF SULFURIC, NITRIC, HYDROCHLORIC, OXALIC, AND CITRIC ACIDS FOR PHOSPHORIC ACID AND POTASH IN SOILS.

In order to gain some information in regard to the relative maximum effect of the acids mentioned above in dissolving phosphoric acid and potash in soils the following experiment was recently conducted:

In order, if possible, to reach the maximum effect of the acids, the digestions were continued at the temperature of boiling water for twenty days. While it may be possible, that in the case of some of the acids employed the solvent action would continue for more than twenty days, especially in the case of potash, it is altogether likely that solution would usually be practically complete far within that time. Loughbridge has shown,¹ for example, that in the case of a soil with which he experimented the solvent effect of hydrochloric acid was complete in five days when the digestion was performed at the temperature of boiling water.

The soil used in this experiment was this year's A. O. A. C., sample No. 1, being a very finely divided clay from the Kentucky Experiment Station farm, proven by several years' trial to contain sufficient available phosphoric acid to grow good crops, but insufficient available potash for that purpose.

¹Amer. Jour. Arts and Sci. 3d ser., Vol. III.

The sulfuric, hydrochloric, and nitric acids used were the concentrated C. P. acids diluted with an equal volume of water.

The oxalic and citric acids contained 10 grams of the crystallized acids in 100 cc of solution. All reagents employed were tested for phosphoric acid and potash.

The results secured are given in Table II. For the sake of comparison, the results secured on this soil by digestion, with some of the acids mentioned, for a different time and under different conditions, are also given:

TABLE II.

Acid used.	Strength of acid.	Time digested.	Temperature at which digested.	Per cent P_2O_5 dissolved.	Per cent K_2O dissolved.
Sulfuric	Sp. gr. 1.548 ..	20 days ..	Boiling water....	.442	.56
Nitric	Sp. gr. 1.260dodo455	.55
Hydrochloric	Sp. gr. 1.094dodo452	.78
Oxalic	10 per cent....dodo455	.50
Citric.....dododo422	.15
$H_2SO_4 + HgO$	Concentrated.	1 hour ..	Boiling H_2SO_4 ..	.442
5 cc H_2SO_4 , 15 cc HNO_3dodo ..	Boiling acids53
HCl.....	Sp. gr. 1.115 ..	10 hours ..	Boiling water....	.425	.30
HNO_3	Concentrated.	48 hoursdo463

By referring to the figures in Table II, it will be seen that in the case of phosphoric acid there was very little difference in the amount dissolved by the different acids. In the case of potash, on the other hand, the difference in the amount dissolved by the different acids is very decided. In general, this is about what has been found by other investigators in the case of different soils. For example, Snyder has shown,¹ in the case of a soil that he treated for only thirty-six hours with a number of acids, that sulfuric, hydrochloric, nitric, and even citric acid removed about the same amount of phosphoric acid, which amount was only a very little less than the total amount present as determined by fusion with alkaline carbonates. In the case of potash, however, the amount removed was quite different with different acids, and in no case was nearly the total amount present.

By referring to the table it will be seen that in the case of this soil one hour's boiling with concentrated sulfuric acid and mercuric oxid dissolved exactly the same amount of phosphoric acid as was dissolved by sulfuric acid in twenty days, and practically the same as was dissolved by the other acids in the same length of time.

By referring to the averages of the A. O. A. C. soil work for 1894, it will also be found that one hour's digestion with sulfuric acid and mercuric oxid dissolved about the same amount of phosphoric acid as two days' digestion with nitric or thirty-six hours' digestion with hydrochloric acid.

Again, by referring to the description of the sulfuric acid method for the determination of phosphoric acid in soils, as outlined by myself in the report of this association for 1894, it will be found that, on the average, one hour's boiling with sulfuric acid and mercuric oxid dissolved practically the same amount of phosphoric acid in the case of a considerable number of soils from several parts of the United States as was dissolved by the usual longer digestions with nitric and hydrochloric acids.

This being the case, the question naturally arises, Why wait thirty-six hours or two days to secure the maximum solvent effect of hydrochloric or nitric acid for phosphoric acid when the same end can be reached in fully as satisfactory a manner with sulfuric acid aided by mercuric oxid in one hour? As a matter of fact, we do not in New Mexico.

¹ Jour. Amer. Chem. Soc., Feb., 1895.

Another very interesting point brought out in this work is the comparatively small amount of potash dissolved in this soil by nitric acid, and the consequent probable indication of the value of that acid as a solvent for available potash.

So much for a brief general consideration of the subject of the determination of phosphoric acid and potash in soils. We will now pass to the consideration of one or two special points in connection with the determination of phosphoric acid.

III.—CONCERNING THE COMPLETENESS OF PRECIPITATION OF PHOSPHORIC ACID IN SOIL SOLUTIONS WITH MOLYBDATE SOLUTION BY THE HIGH TEMPERATURE AND SHORT TIME METHOD OF PRECIPITATION.

It has been stated that small amounts of phosphoric acid can not be completely precipitated from soil solutions in so short a time as twenty-five minutes. In order to further test this point, the following experiment was tried:

To portions of 100 cc each of the filtrate from the phosphoric acid determination in soil No. 1 were added known amounts of phosphoric acid in the form of sodium phosphate, and the precipitation made as before. The utmost care was taken to secure filtrates for this work as free from phosphoric acid as it was possible to get them. There was none of that substance remaining which could be precipitated with molybdate solution, either in the bath at a high temperature or upon standing forty-eight hours.

To the first portion of 100 cc was added an amount of P_2O_5 corresponding to 0.01 per cent in an actual determination where 4 grams of soil is taken. The second portion received an amount corresponding to 0.10 per cent and the third to 0.50 per cent. The precipitations were made in the bath at 80° in fifteen minutes, as usual, and allowed to settle for ten minutes before filtering. An additional amount of molybdate solution was added to each sufficient to make the total amount present about 75 cc.

As a check on the absence of phosphoric acid in the solutions, portions of 100 cc each of distilled water containing 0.01 per cent of P_2O_5 were precipitated in the same manner.

In all cases the yellow precipitate formed very promptly, and so far as general appearance was concerned the precipitation was entirely satisfactory. The reagents used were proven free from phosphoric acid. The results secured are given in Table III:

TABLE III.

Cc H_2O taken.	Cc soil filtrate taken.	Grams P_2O_5 added.	Per cent P_2O_5 added, calculated to 4 grams.	Grams P_2O_5 recovered.	Per cent P_2O_5 recovered, calculated to 4 grams.	Per cent P_2O_5 recovered in excess of that added.	Per cent P_2O_5 insoluble in ammonia.
100	0.0004	0.010	0.0006	0.015	0.005
.....	100	.0004	.010	.0007	.017	.007
.....	100	.0040	.100	.0041	.104	.004	0.005
.....	100	.0200	.500	.0204	.510	.010	.056

By referring to the figures in Table III, it will be noticed that the results in each case instead of being low are slightly high, and it is my opinion that, as a rule, there is more danger of getting high than low results in precipitating the phosphoric acid in soil solutions. This statement, I believe, applies not only to the high temperature method of precipitation, but to precipitation in the cold or at any temperature below 80° , provided the same be complete. With experience and care, however, I am sure results can be uniformly obtained which will be very nearly correct. The greatest difference in any case between the amount found and the amount actually present was but .01 per cent in the case of the solution containing an amount equivalent to .5 per cent—an amount insufficient to have any practical bearing on the interpretation of results.

As to the completeness of the precipitation of small amounts of phosphoric acid in fifteen minutes at 80° , I can only repeat, after another year's work, that I have yet to find a single example to the contrary where the essential conditions of the precipitation are correct.

IV.—COMPARISON OF THE HIGH TEMPERATURE AND SHORT TIME METHOD OF PRECIPITATING PHOSPHORIC ACID IN SOIL SOLUTIONS WITH THE LOW TEMPERATURE AND LONG TIME METHOD.

In many of the directions for precipitating phosphoric acid in soil solutions with molybdate solution the use of a comparatively low temperature is called for.

Under such conditions, if the solution be very dilute, it is necessary to allow twelve hours, or in exceptional cases double that time or more, for complete precipitation. In more concentrated solutions the time necessary for complete precipitation is considerably less, but even then several hours are found to be necessary in the case of soil solutions.

It has also been stated that in solutions containing much aluminium the precipitation of phosphoric acid with molybdate solution can not be safely accomplished at a high temperature, owing to the fact that under such conditions the precipitate is liable to carry down aluminium, to avoid which it is necessary to make the precipitation at a low temperature.

As aluminium is practically always present in acid solutions from soils, and is undoubtedly sometimes carried down from such solutions when precipitating phosphoric acid with molybdate solution, rendering impossible the complete solution of the phosphoric acid when dissolving the yellow precipitate in ammonia, it has seemed to me to be of sufficient importance to make a further study of the matter in connection with this year's soil work.

The results secured on the above points are given in Table IV:

TABLE IV.

	Samples.					Average.
	No. 1.	No. 2.	No. 3.	No. 4.	No. 120.	
Solution by 1 hour's boiling with H_2SO_4 and HgO :	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>
P_2O_5 precipitated in fifteen minutes at 80°	0.442	0.249	0.438	¹ 0.253	0.057	0.319
P_2O_5 insoluble in ammonia when dissolving yellow precipitate042	.011019
P_2O_5 from same solution precipitated hot in beaker, stood in cold twenty-four hours.....	.439	.249	.422	¹ .216	.041	.315
P_2O_5 insoluble in ammonia064	.015030
P_2O_5 from same solution precipitated cold stood in cold forty-eight hours.....	.436
P_2O_5 insoluble in ammonia.....	.057
Solution by ten hours' digestion with HCl at 100° :						
P_2O_5 precipitated in twelve hours at 40°425	.163
P_2O_5 insoluble in ammonia011	.008
P_2O_5 from same solution precipitated in fifteen minutes at 80°412
P_2O_5 insoluble in ammonia.....	.005

¹ Not included in the average.

In referring to the figures in Table IV it will be seen, in the first place, that rapid precipitation at a high temperature gave practically the same results as slow precipitation at a low temperature so far as the total amount of phosphoric acid is concerned.

In regard to the amount of phosphoric acid left upon dissolving the yellow precipitate in ammonia, it will be seen that the slow precipitation at a low temperature, instead of giving less, actually gave somewhat more. It would seem then that slow precipitation at a low temperature is not only no better in this respect than rapid precipitation at a high temperature, but is, as a matter of fact, not quite so good. I believe this result to be due, in part at least, to the fact that, in the slow precipitation, the precipitate adheres to the sides of the vessel in which the precipitation is made much worse than in the case of rapid precipitation, thus making the thorough washing of the precipitate more difficult.

It will be noticed that the solution obtained by ten hours' digestion with hydrochloric acid gave a slight insoluble precipitate as well as the sulfuric acid solution, and it has been my experience that nitric acid solutions also sometimes give the same trouble. As would naturally be expected, the solution obtained by one hour's boiling with concentrated sulfuric acid gave somewhat more of this insoluble precipitate than the solution obtained by ten hours' treatment with hydrochloric acid. This is probably due to the greater amount of aluminium present in the sulfuric acid solution.

A second precipitation is necessary, however, in either case whenever the insoluble precipitate is present in any considerable quantity, so that so far as this point is concerned it makes practically very little difference whether the solution is made with sulfuric, hydrochloric, or nitric acid.

By referring to Table III, it will be seen that the same insoluble precipitate was present upon adding phosphoric acid to a soil solution from which the phosphoric acid had already been precipitated and precipitating a second time. From the results given in Table III, it would also seem that the amount of insoluble precipitate is, in the same solution, in a rough way proportional to the amount of phosphoric acid present.

Incidentally, a striking example of the long time necessary for the complete precipitation of phosphoric acid in dilute soil solution upon standing in the cold, was furnished in this work.

By referring to Table IV, it will be seen that, in the case of soil No. 4, the amount secured by precipitation in the cold was considerably less than by the high temperature precipitation. This particular solution did not stand as long as the other, and after filtering off the precipitate a further precipitate formed in the filtrate upon standing. This was not added to the first amount, which accounts for the low results in this case.

Unfortunately a close record was not kept of the time this series of solutions stood to precipitate, as this point was not under observation at the time. There is no doubt, however, in regard to the statement that in the case of soils Nos. 1, 2, and 3 the solutions stood more than twenty-four hours to precipitate, and no further precipitation occurred in the filtrates, while in the case of No. 4 the solution stood between twelve and twenty-four hours, and the precipitation was incomplete. As this determination, as well as most of the others recorded in this table, was made in duplicate, there is little probability of a mistake as to the facts in the case.

In conclusion, I will say that in the case of soil work I am very decidedly in favor of the quick precipitation of phosphoric acid at a high temperature. To be sure, a little experience may be necessary in order to become familiar with the essential conditions of the high temperature precipitation; but, then, experience is an essential condition of success with any analytical method.

MR. WILEY. I have a letter from Mr. E. W. Hilgard, in which he asks me to present his paper on the deficiency of nitrogen in soils.

THE RECOGNITION OF "NITROGEN HUNGRINESS" IN SOILS.

By E. W. HILGARD.

The determination of nitrates and ammonia salts in soils ordinarily conveys little information concerning their resources in nitrogen for plant supply. A soil may at certain seasons be found totally wanting in these compounds, and may yet be able to yield to crops under proper conditions all the nitrogen required. So variable and minute are the amounts usually present that their determination is mostly of little practical interest.

The permanent or "reserve" supply of soil nitrogen is unquestionably that contained in the humus, in the (supposed) amidic form, which is gradually made available by the nitrifying organism, when the favoring conditions of moisture, warmth, and access of oxygen are fulfilled, in connection with the neutral (or basic) condition of the soil, due to the presence of an excess of earthy carbonates.

It is a priori probable that the composition of the complex and indefinite substance we call humus must exert a material influence on the rate of nitrification. It is known that when it is in an acid condition, nitrification is almost null. It seems at least likely that the process is also affected by the richness of the humus in nitrogen, which has all along been known to be indefinite, but has usually been assumed to range from about 3 to 5 per cent.

I have in former papers¹ called attention to the fact that the only reasonably reliable method for the determination of true humus in soils is that of Grandean, viz, extraction of the humus with weak alkaline lye, after setting it free from its earthy combinations by treatment with weak HCl. All combustion methods, whether in the wet or in the dry way, as well as extraction with strong lye, yield utterly indefinite results, on account of the simultaneous combustion or dissolution of unhumified matter, varying with the seasons and the crop. It is only with the substance ("matière noire") extracted by Grandean's process that definite and consistent results can be obtained.

In the paper quoted above I have given a summary of the results of investigations made by Jaffa and myself on the marked differences in the nitrogen contents of humus in the arid and humid regions, showing that while in the soils of the latter the average percentage is less than 5 and rarely exceeds 6, in arid soils the average percentage is over 15, and in some cases approaches 19, being several per cent higher than in the albuminoids.

It can hardly be doubtful that such differences in nitrogen content must materially influence nitrification. The nitrifying organism requires oxygen to accomplish its life process. The supply of that element in the soil is limited, and if in one case nineteen out of twenty, in the other case only four out of five, parts of carbohydrate substance has to be oxidized away to get at one part of nitrogen, it can hardly be doubtful which will lend itself most readily to the nitrifying process. As a matter of fact, the constant occurrence of nitrates in the soils of the arid region, poor as they usually are in humus, establishes this a priori presumption.

In view of these facts, it seems highly probable that *there is a certain minimum of nitrogen percentage in humus below which the nitrifying organism will be incapable of sufficiently intense action to supply the current demands of crops.* If this is true, then we have in the determination of the nitrogen percentage of humus the means of determining whether or not a soil is in need of a supply of available nitrogen for crop production—whether or not it is "nitrogen hungry."

I have during the past year pursued the investigation of this subject with the aid of Mr. Jaffa, and find, so far as we have gone, the above presumption is fully verified.

¹ On the Nitrogen Contents of Soil Humus (Agr. Sci., April, 1894; Wollny's Forsch. Agr. Phys. Bd. 19 S., 478; Ann. Sci. Agr., 1892, p. 297).

A topical review of some of our results was communicated at the Denver meeting of the Association of American Agricultural Colleges and Experiment Stations, and will be published in detail elsewhere. For my present purpose it is sufficient to give some summary statements, in order that the subject may be taken in hand by members of this body whose opportunities for the investigation of exhausted soils are better than those existing in California. In fact, our most decisive observations have been made on soils from the Hawaiian Islands, for lack of home material. Some illustrations may be of interest.

In one of the soils of the home station, which in the virgin condition shows humus containing over 18 per cent of nitrogen, we find, after twelve years of exhaustive cultivation in grass, with a very slightly increased humus percentage (1.6 against 1.4 at first), only 3 per cent of nitrogen in that humus, being a decrease in the total nitrogen of the soil of 15 per cent. The grass was taken up because of its failure to make a satisfactory growth. In this case, it is true, a determination of the total

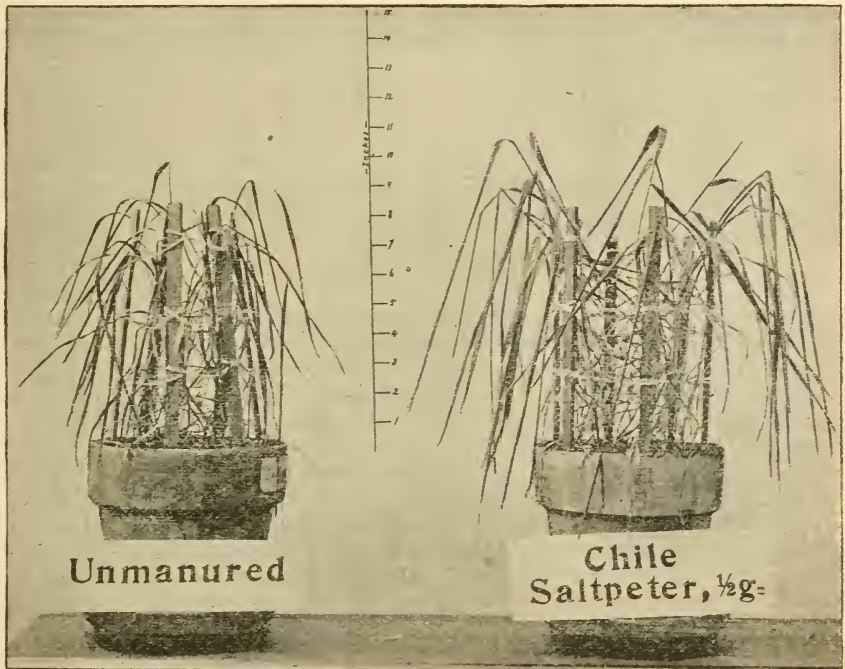


FIG. 1.—Result of adding a nitrogenous fertilizer to a nitrogen-hungry soil.

nitrogen of the soil would at once indicate a probable deficiency. In another plot of the same soil, which had been set in ramie for about ten years, the nitrogen percentage was found to be reduced to 5 per cent.

But perhaps the most striking case is that of a soil from Hawaii, which showed 10 per cent of humus by Grandeau's method. It was almost virgin land, just cleared of gnava brush, but had borne one good crop of sugar cane and one fair one of ratoons. The third year, the cane freshly planted refused to grow after having exhausted the seed cane; and from the symptoms reported I was inclined to diagnose deficiency of nitrogen, before the humus determination was made. On determining the nitrogen in the humus it was found to be only 1.7 per cent, the lowest that has come under my observation thus far.

Having previously come to the conclusion that any soil containing humus with much less than 2.5 per cent of nitrogen was to be suspected of "nitrogen hungeriness," and notwithstanding that the total nitrogen percentage in this soil (0.17 per cent) might be considered a high one, I recommended the use of nitrogenous fertilizers; and also made a pot-culture experiment with the same soil, using about a kilogram in each pot, and fertilizing one with half a gram of Chile saltpeter.

The subjoined illustration (fig. 1) shows the result of this experiment at a time when an overwhelming attack of mildew (of a species not heretofore observed here) put an end to it. There can be no question of the result, as showing deficiency of available nitrogen. According to late information from Hawaii, corresponding results have been obtained in the field with cane manured with Chile saltpeter, notwithstanding the fact that an unusually wet season was most unfavorable to the efficacy of that salt.

I therefore suggest that this association place on its programme for the coming year an investigation of this interesting question, which, in connection with the method of Dyer for the determination of available phosphoric acid and potash, promises to put us in possession of the long-sought means for estimating the immediate productive power of soils, as contradistinguished from the determination of the reserve of plant food, and therefore of their probable durability by extraction with strong acids.

The PRESIDENT. I think we would be interested to hear from Mr. Whitney, of the Division of Soils, Agricultural Department, who is present, if he will so favor us.

REMARKS OF MR. WHITNEY.

MR. WHITNEY. Mr. Chairman and gentlemen, I shall be glad to say a few words in regard to the methods of the physical analysis of soils and the physical determinations that should be made in connection with chemical work. I do not want to bring up the relative importance of the physical and chemical work here, but I do want to insist upon the importance of physical work accompanying at all times the chemical determinations.

It seems to me that many of the details of the physical examination of soils in common use in this country and some of those adopted by this association have no practical value, and are therefore useless, as we are not able to interpret the results. The determination of the hygroscopic moisture, the water-holding power, the capillary power, the specific gravity, and the specific heat, as ordinarily determined and applied, have no practical value, for we are unable to understand or interpret the results. They certainly seem to have no direct bearing at present upon practical agriculture.

I think that if the association would consider first the physical conditions which are known to affect plant growth, and would adopt suitable methods for their determination so that the results of different observers and in different soils would at least be comparable, it would be very much better, and then these other physical properties of soils could be taken up as their value was seen and as it was necessary for the explanation of various phenomena.

The most important conditions that occur to me as existing in the soil and having a very marked influence upon the determination of crops are the conditions of moisture, the circulation of air, and the temperature of the soil in which the crops are grown. The relation of soil to moisture is in my judgment by far the most important of these, although it is complementary to the relation of the soils to air, and the determination of one carries with it almost the determination of the other.

The relation of soils to water depends as I have shown elsewhere upon five factors: The volume of space; the texture or the relative amount of sand, silt, and clay; the structure or the relative arrangement of the soil grains; the amount and char-

acter of the organic matter, and the depth of the soil. I think the association will do well to limit its methods for the present to the determination of the texture and structure of soils and to actual moisture determinations in the field.

The texture of the soil should be determined by a mechanical analysis. There are two methods for this in use in this country—Hilgard's elutriator method and Osborne's beaker method. Personally I prefer the latter on account of its simplicity, the small cost of the outfit, and the control one has of the operation. I believe, however, that the two methods give results which agree within the limits of error of either one, and that they should both be adopted by the association, but that a statement should always be made as to which method was used in an analysis.

The structure of the soil, or the relative arrangement of the soil grains, should be determined by the rate of flow of some fluid (probably either water or air) through a given volume of soil. This necessitates the determination of the volume of space which can be found either by direct determination or, preferably, by the difference between the real and apparent specific gravity of the soil. No satisfactory method has yet been devised for determining the structure of soils, principally on account of the difficulty of taking samples from the field that will give accordant results, and the difficulty of manipulating the air-dry samples so as to secure uniform conditions throughout the mass which will give accordant results in a series of determinations.

A method should certainly be adopted by this association for the determination of the amount of moisture in the field, and daily records over at least a part of the growing season should be insisted upon as a very essential factor in the study of the physical conditions and properties of a soil. The only method I know of at present adapted to this purpose is to take a sample of soil in a tube of suitable size and uniform depth, preserve it carefully from loss through evaporation, and make an ordinary moisture determination in the sample by drying at a suitable temperature to constant weight. I use a sample of about 100 grams, and dry in an aluminium dish for twenty-four hours at a temperature of 110°. The time differs somewhat, of course, according to the texture of the soils. This method is bulky and troublesome, and is not very accurate on account of the difficulty of taking samples from the field which will give accordant results. The method is far better than none, however, and the results when averaged are comparable for different localities. These moisture records form a most important feature of the physical analysis of soils, as it shows the actual amount of moisture at the disposal of the crops, yet it is rarely included in our soil investigations. It will be found that the different soils in which you are interested are likely to maintain very different quantities of water at the disposal of crops, owing either to the difference in texture or a difference in structure or to some other condition, and that in many cases it is this relation of the soil to water and the amount which it maintains which determines the peculiar agricultural value of the land.

The relative temperature of different soils should be determined with registering maximum and minimum soil thermometers.

The Division of Agricultural Soils has nearly perfected an entirely new method of determining the amount of moisture in the soil of a field and a new method of determining the temperature of soils, and we hope before long to publish these methods for the information of all interested in the material advancement of agricultural methods.

SECOND DAY.

FRIDAY—MORNING SESSION.

The president called the meeting to order at 9 a. m., and asked for the report on phosphoric acid, which was presented by Mr. Kilgore.

REPORT ON PHOSPHORIC ACID.

By B. W. KILGORE.

About the 25th of November, 1894, a letter was addressed to various official, commercial, and other chemists, soliciting their cooperation in the phosphoric acid work for the Association of Official Agricultural Chemists for 1895, and asking for the suggestion of points deemed worthy of investigation, and their methods of carrying out such investigations. After considering these replies, the literature on recent phosphoric acid work, and the suggestions made to the reporter at the last meeting of the association, a set of three samples was prepared and sent to all chemists requesting them (forty-five), with the following instructions:

INVESTIGATION OF METHODS FOR DETERMINING PHOSPHORIC ACID FOR THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1895.

Three samples have been prepared for use in this investigation.

No. 1 is a phosphate solution, slightly acid with nitric acid, and containing in 50 cc the equivalent of about 20 per cent P_2O_5 on basis of 0.5 gram substance.

No. 2 is a dilute phosphate solution, slightly acid with nitric acid, and containing in 50 cc the equivalent of 3 to 3.5 per cent P_2O_5 on basis of 0.5 gram substance. These solutions were made up at 54° F.

No 3 is a mixed fertilizer.

In bottle No. 4 is standard potassium hydroxid, free from carbonates, 1 cc of which equals, according to my analysis, 1 milligram P_2O_5 (1 per cent P_2O_5 on basis of 0.1 gram substance). One hundred cc of this solution will neutralize 32.37 cc of normal acid, and can be made by diluting 323.7 cc of normal potassium hydroxid, which has been freed from carbonates by barium hydroxid, to 1,000 cc. The acid of corresponding strength to be used in titrating against this can be made in a similar way from normal acid. Hydrochloric or sulphuric acids will answer for this purpose, but nitric acid is to be preferred.

The following plan is outlined for the investigations:

1. *The determination of phosphoric acid gravimetrically.*—Determine total phosphoric acid in all three samples and insoluble in No. 3 (and also citrate soluble in No. 3, where this line of the investigation is taken up) (a) according to the official methods (Bull. 43, Div. Chem., U. S. Dept. Agr., p. 341), and (b) according to the official methods to the point of dissolving the "yellow precipitate," which dissolve in 2.5 per cent NH_3 ; do not use any water, and only enough ammonia wash to insure complete removal of phosphomolybdate of ammonia from the filter. Precipitate at once, without neutralizing, (c) by adding 20 cc of magnesia mixture No. 1 to sample No. 1, 15 cc to total of No. 3, and 10 cc to total of No. 2, and insoluble and reverted of No. 3; and (d) precipitate a second series of solutions with like amounts of magnesia mixture No. 2. Magnesia mixtures Nos. 1 and 2 should be added at once and as quickly as possible with stirring. After fifteen minutes add 25 cc 0.90 sp. gr. ammonia and (e) let it stand three hours; (f) make a second set of determinations in the same way and let stand five hours, or over night if more convenient. In the determinations under (a), where the official magnesia mixture is used, allow the "white precipitates" to stand the same length of time as under (c) and (f), where the new magnesia mixtures are used. Report number of cubic centi-

meters of official magnesia mixture used in each case. Filter, wash the "white precipitates" until practically free of chlorids; dry, and burn to whiteness, or to a grayish white, and note whether there is any difference in burning to whiteness and as you usually burn.

The magnesia mixtures are made as follows:

No. 1. Magnesium chlorid.....	grams..	110
Citric acid.....	do.....	200
Ammonia, sp. gr. 0.96.....	cubic centimeters..	1,000
Water to make up to.....	do.....	2,000
No. 2. Magnesium chlorid.....	grams..	110
Citric acid.....	do.....	100
Ammonia, sp. gr. 0.96.....	cubic centimeters..	750
Water to make up to.....	do.....	2,000

Dissolve the citric acid in the ammonia, and the magnesium chlorid in a small amount of water; mix, and make up with water to the required volume.

2. *Volumetric determination of phosphoric acid.*—Make solution of No. 3 by the nitric and hydrochloric acids method (4) for total and dilute to 200 c. c. Measure out 20 cc for totals in Nos. 1 and 3, and 40 cc for total in No. 2 and insoluble in No. 3; add about 5 cc strong nitric acid to total and insoluble solutions of No. 3, and 7 to 10 cc to solutions Nos. 1 and 2; add ammonia until precipitate just begins to form; dilute total solutions of Nos. 1 and 3 to about 100 cc, and total and insoluble solutions of Nos. 2 and 3, respectively, to 60 or 75 cc; digest in water bath at 60° C. (60° in bath equals about 55° in beaker), and after filtering the molybdate solution indicated below add 30 cc to totals of Nos. 1 and 3, and 10 cc to total of No. 2 and insoluble of No. 3; allow to stand four to five minutes from the time the molybdate is added, and filter as quickly as possible upon a 3-inch Hirsch funnel, whose perforations are covered with a disk of soft filter paper, or upon a filter made by putting a platinum cone or disk, well filled with holes, into a 3-inch funnel, and covering with coarse asbestos, using filter pump in both cases. Filter paper may be used, but the other filters in the order named are much preferred. It is specially urged that the 3-inch Hirsch funnel be gotten, where it is possible, as it permits of rapid filtration and easy and thorough washing. By using this funnel a half dozen filtrations can be easily completed in from six to eight minutes from the time the molybdate solution is added. Wash the precipitate twice by decantation with dilute nitric acid, using 50 to 75 cc each time, and agitating thoroughly, once by decantation with the same amount of 3 per cent potassium nitrate, then onto the filter and with 300 to 500 cc (about 400 cc) water, or until no longer acid. Wash the precipitate with filter back into the beaker, titrate with potassium hydroxid. and back with nitric acid, using about 1 cc of phenolphthalein (1 gram in 100 cc alcohol) as indicator, and adding acid until color disappears.

The above instructions apply especially to the samples sent out. It is requested that you also test this method, where possible, on samples you have already or are analyzing in your laboratory by the gravimetric method. For regular fertilizer work follow instructions for total and insoluble in No. 3. Dissolve in nitric and hydrochloric acids, make up to 200 cc, measure out 20 cc for total and 40 cc for insoluble (or percentages below 5 or 6) corresponding to 0.2 and 0.4 gram substance, respectively; add about 5 cc strong nitric acid and then ammonia until precipitate just begins to form; dilute totals to about 100 cc and insolubles to 60 to 75 cc, and precipitate and carry out as above indicated, not using any greater excess of molybdate than is necessary to insure complete precipitation.

On washing by decantation, if the precipitate is allowed to completely settle each time, no trouble will be experienced in the after washing.

The solutions to be used in the above work are:

Molybdc solution.—To 100 cc of the regular official molybdate add 5 cc 1.42 sp. gr. nitric acid. This solution should be filtered each time before using.

Dilute nitric acid wash.—Dilute 100 cc 1.42 sp. gr. nitric acid to 1,000 cc.

In this connection it will be interesting to consult the "Report on phosphoric acid" to the A. O. A. C. for 1894 (Bul. 43, Chem. Div. U. S. Dept. Agr., p. 68), and Jour. Am. Chem. Soc., 15, 7, p. 382, and 16, 11, p. 765, 1894.

3. The method proposed by Professor Ross (La. Expt. St. Bul. No. 22, pp. 745-746; Buls. 38 and 43 U. S. Dept. Agr., pp. 16-68) for the "direct determination of citrate-soluble phosphoric acid" in the ammonium citrate filtrate. The method is as follows: "After completion of the thirty minutes' digestion of the sample with citrate solution, filter out at once into a dry vessel 25 cc of the solution; if the liquid is filtered directly into a dry burette (or measuring flask) 25 cc can be readily transferred to another vessel without dilution. After cooling, run 25 cc of the solution into a digestion flask of 250-300 cc capacity, add about 15 cc of concentrated sulphuric acid, and place the flask on a piece of gauze over a moderately brisk flame;

in about eight minutes the contents of the flask commence to darken, and foaming begins, but will occasion no trouble if an extremely high or a very low flame are avoided. In about eleven to twelve minutes the foaming ceases, and the liquid in the flask appears quite black; about 1 gram of mercuric oxid or metallic mercury is now added, and the digestion continued over a brisk flame until the liquid is colorless. After cooling, the contents are washed into a beaker, and the determination continued as under total P_2O_5 .

In working this method, add the full amount of ammonium nitrate (15 grams) before precipitating with molybdate, and allow molybdate precipitate to stand one hour at 65° .

To test this method you are requested to determine citrate soluble in No. 3 (a) as above described, and (b) by evaporating the same amount of the ammonium citrate filtrate used in (a) to dryness and gently igniting in presence of magnesium nitrate; also by adding 10 cc solution No. 1 to 25 cc ammonium citrate solution and (1) treating as in (a) above, and (2) treating as in (b).

Please determine soluble and insoluble in No. 3, and report citrate soluble by difference.

See in connection with this method the "Report on phosphoric acid" (Bul. 43, Div. Chem., U. S. Dept. Agr., p. 71). The results here presented are not at all satisfactory, and it is feared that they will be of the same kind this year, as no improvement is offered in the method. It is therefore requested that any one who can devise a new method, or offer a modification to the present one that will accomplish the object intended will do so, and spend his time in investigating this instead of the method sent out.

Please report results by the gravimetric method for total on solutions 1 and 2 in terms of weight of magnesium pyrophosphate in 50 cc or 50 grams, and for the citrate soluble investigation on No. 1 report the magnesium pyrophosphate in 10 cc or 10 grams. State whether the "white precipitates" were washed free of chlorids, and the amount of wash solution required with the different magnesia mixtures.

In your work on the volumetric method, please report amount of substance used for analysis, kind of filter used, amount of washings, and any other points of interest coming under your observation. Report all results in terms of my alkali and the strength of your alkali in terms of number of cc corresponding to 100 cc of mine. Give results by volumetric method on solutions 1 and 2 in terms of cc of alkali required to neutralize the ammonium phosphomolybdate from 20 cc or 20 grams of No. 1, and 40 cc or grams of No. 2.

Should you not have time to investigate all the points outlined, take up those of most interest to you. The reporter will be pleased to receive other data than that asked for, and will give full credit in report for all such.

A thorough study of one or more of the subjects is much to be preferred to a small amount of work on all, and as two or three samples are not sufficient to test a method, you are requested to use as many samples of different kinds as possible. It is also requested that determinations be made in duplicate at least, and that any deviation from the methods outlined be reported.

TO WHOM SAMPLES WERE SENT.

The phosphoric acid samples were sent to 23 chemists connected with agricultural experiment stations, agricultural colleges, and universities, 1 to the Department of Agriculture at Washington, 1 to the United States Geological Survey, 10 to European chemists, 1 to Canada, and 9 to commercial chemists, making 45 in all. Reports have been received from the Department of Agriculture, 2 from foreign chemists, and 11 from experiment stations and colleges, including the work of 22 chemists.

The data obtained will be considered under four heads.

I. GRAVIMETRIC DETERMINATION OF PHOSPHORIC ACID—COMPARISON OF MAGNESIA MIXTURES—OBJECT.

The work of this association last year showed that our official molybdate magnesia method gives high results.¹ This same observation has been made by quite a number of other analysts. Dr. S. W. Johnson, in a summary statement of results² by different methods, has shown that the official method gave high results on a phos-

¹ For summary of this work see Jour. Am. Chem. Soc., XVI, p. 793, and Bul. 43, Div. Chem., U. S. Dept. Agr., p. 80.

² Jour. Am. Chem. Soc., XXI, 462.

phate of known content of phosphoric acid, and likely gave high results on a great many others whose content was not definitely known. If iron, alumina, or manganese be present, and the temperature of precipitation be as high as 65° C., the results, he states, are too high. In the same communication he states that the citrate method gives good results as compared with the molybdate method "by compensation of its errors;" some of the phosphoric acid remains unprecipitated, while the precipitate may be contaminated with carbon, silica, calcium, iron, and aluminum. This work was upon ordinary phosphates and fertilizers, containing various impurities. On the other hand, N. von Loreuz,¹ working upon a chemically pure mono-ammonium phosphate, obtained theoretical results by adding 2 per cent of citric acid to the ammoniacal solution of the ammonium phosphomolybdate before adding magnesia mixture.

With the official method giving too high results and the citrate method seemingly not possessing any advantages over the official, as regards accuracy at least, it occurred to the reporter that von Lorenz's procedure of adding citric acid to the alkaline solution of the phosphomolybdate, either alone or in the magnesia mixture, might add to the accuracy of the official method. With this end in view magnesia mixtures were made, in which 25 to 100 grams to the liter of citric acid replaced wholly or in part the ammonium chlorid of the official magnesia mixture. In all, six of these mixtures were tried in the laboratory of the North Carolina Experiment Station before making up the instructions to be sent out, using a c. p. di-sodium hydrogen phosphate containing 19.826 per cent P_2O_5 for the investigation. Mixtures 1 and 2, whose formulas are given in the instructions, gave the most satisfactory results. These results are presented in the following table:

Magnesia mixtures.	Cc 0.96 sp. gr. NH_3 added after precipitating.	Cc 0.90 sp. gr. NH_3 added after precipitating.	"Yellow precipitate" dissolved in per cent NH_3 .	Analysts.			
				Kilgore.	Carpenter.	Allen.	Williams.
				<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
No. 1.....	30	-----	2.5	19.82	-----	19.89	-----
				19.83	-----	19.75	-----
	-----	25	2.5	19.77	19.63	$\left\{ \begin{array}{l} 19.93 \\ 19.77 \\ 19.777 \end{array} \right\}$	$\left\{ \begin{array}{l} 19.78 \\ 19.68 \end{array} \right\}$
No. 2.....	30	-----	2.5	19.93	-----	-----	-----
				19.96	-----	-----	-----
	-----	25	2.5	19.89	19.93	$\left\{ \begin{array}{l} 19.75 \\ 19.92 \\ 19.77 \end{array} \right\}$	$\left\{ \begin{array}{l} 19.91 \\ 19.80 \\ 19.98 \end{array} \right\}$

From this table it will be seen that the results with magnesia mixtures Nos. 1 and 2 generally agree fairly well with the theoretical percentage of this salt. They are nearer the theory than the results obtained at the same time with the official magnesia mixture. On the basis of these results mixtures 1 and 2 were thought to indicate well, and were sent out on this ground.

RESULTS FOR COMPARISON OF MAGNESIA MIXTURES.

The results of the different analysts for the comparison of magnesia mixtures 1 and 2 with the official magnesia mixture on the samples sent out by the reporter are brought together in Table I. These results are the averages of from two to six determinations by each analyst. The averages of all results and variations from them were made up from the several results of all analysts.

¹Zeitschrift f. anal. Chemie, XXXII, 64.

TABLE I.—Comparison of magnesia mixtures.

Analyst.	Official magnesia mixture.	Magnesia mixture No. 1.		Magnesia mixture No. 2.	
	Total P ₂ O ₅ .	Total P ₂ O ₅ .	Differ- ence, greater (+) and less (—), than official.	Total P ₂ O ₅ .	Differ- ence, greater (+) and less (—), than official.
<i>Reporter's sample No. 1.</i>					
<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
F. B. Bomberger, Maryland Agricultural College...	20.01	19.82	—0.20	19.92	—0.09
Maurice Bird, Louisiana Experiment Station.....	20.42	20.00	— .42	20.12	— .30
C. L. Sargent, Rhode Island Experiment Station...	20.13	18.98	—1.15	19.44	— .69
W. M. Cobleigh, Montana Experiment Station.....	20.23	20.10	— .13	20.60	+ .37
F. W. Traphagen, Montana Experiment Station....	20.31				
John P. Street, New Jersey Experiment Station....	20.04	19.98	— .06	19.98	— .06
W. A. Power, Illinois Experiment Station.....	19.89	19.81	— .08	19.88	— .01
R. G. Newborne, North Carolina Agricultural Col- lege	19.97	19.42	— .55		
E. G. Runyan, United States Department of Agri- culture	19.78	19.94	+ .16	19.94	+ .16
W. M. Allen, North Carolina Experiment Station...	19.94	19.58	— .36	19.57	— .37
C. B. Williams, North Carolina Experiment Station.	19.91	19.69	— .22	19.90	— .01
F. B. Carpenter, North Carolina Experiment Sta- tion	19.83	19.69	— .14	19.93	+ .10
B. W. Kilgore, North Carolina Experiment Station.	19.95	19.49	— .46	19.54	— .41
H. E. Curtis, Kentucky Experiment Station.....	¹ 19.96				
Average	20.04	19.70		19.86	
Theory	19.826	19.826		19.826	
Variations between highest and lowest results.....	.75	1.53		1.37	
Variations of highest results above theory.....	.674	.314		.884	
Variations of lowest results below theory.....	.076	1.216		.496	
<i>Reporter's sample No. 2.</i>					
F. B. Bomberger, Maryland Agricultural College..	3.41	3.52	+ .09	3.42	+ .01
Maurice Bird, Louisiana Experiment Station.....	3.43	3.29	+ .14	3.35	— .08
Duncan Adriance, Texas Agricultural College.....	3.37	3.41	+ .04	3.42	+ .05
C. L. Sargent, Rhode Island Experiment Station...	3.38	3.29	— .09	3.31	— .07
W. M. Cobleigh, Montana Experiment Station	3.51	3.50	— .01	3.59	+ .08
F. W. Traphagen, Montana Experiment Station ...	3.54				
John P. Street, New Jersey Experiment Station...	3.48	3.30	— .18	3.43	— .05
W. A. Power, Illinois Experiment Station.....	3.54	3.35	— .19	3.37	— .17
R. G. Newborne, North Carolina Agricultural Col- lege	3.28			3.29	+ .01
E. G. Runyan, United States Department of Agri- culture	3.34	3.22	— .19	3.28	— .06
W. M. Allen, North Carolina Experiment Station ..	3.39			3.16	— .23
B. W. Kilgore, North Carolina Experiment Station.	3.37	3.28	— .09	3.28	— .09
H. E. Curtis, Kentucky Experiment Station.....	¹ 3.36				
Average	3.43	3.34		3.35	
Theory	3.304	3.304		3.304	
Variations of lowest results below the theory.....	.104	.284		.194	
Variations of highest results above the theory....	.346	.276		.346	

¹ Results received too late to be included in averages.

TABLE I.—Comparison of magnesia mixtures—Continued.

Analyst.	Official magnesia mixture.	Magnesia mixture No. 1.		Magnesia mixture No. 2.	
	Total P ₂ O ₅ .	Total P ₂ O ₅ .	Differ- ence, greater (+) and less (—), than official.	Total P ₂ O ₅ .	Differ- ence, greater (+) and less (—), than official.
<i>Reporter's sample No. 3.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
F. B. Bomberger, Maryland Agricultural College...	12.55	12.40	— .15	12.72	+ .17
C. L. Sargent, Rhode Island Experiment Station....	12.51	11.92	— .59	12.02	— .49
W. M. Cobleigh, Montana Experiment Station.....	12.98	12.76	— .22	13.48	+ .50
F. W. Traphagen, Montana Experiment Station....	13.12	12.73	— .34	13.22	+ .10
John P. Street, New Jersey Experiment Station....	12.74	12.54	— .20	12.75	+ .01
W. A. Power, Illinois Experiment Station.....	12.31	12.55	+ .24	12.44	+ .13
R. G. Newborne, North Carolina Agricultural Col- lege	12.22	12.17	— .05
Eskidge and Elliott, Virginia Agricultural College..	12.48	12.19	— .29
E. G. Rnnyan, United States Department of Agri- culture	12.48	11.54	— .94	12.30	— .18
W. M. Allen, North Carolina Experiment Station...	12.55	12.31	— .24
H. E. Curtis, Kentucky Experiment Station	12.49
Average.....	12.66	12.43	12.57
Greatest variation from mean.....	+ .57	— .78	+ .93
Variation between highest and lowest results.....	1.05	1.27	1.54

¹ Results received too late to be included in averages.

COMMENTS OF ANALYSTS UPON THE DETERMINATION OF PHOSPHORIC ACID GRAVIMETRICALLY AND UPON THE NEW MAGNESIA MIXTURES NOS. 1 AND 2.

F. B. Bomberger, Maryland.—All the magnesium ammonium phosphate precipitates, except the insoluble of No. 3, were washed with 300 cc of 2½ per cent ammonia, which was found sufficient to practically free them of chlorids. Insoluble of No. 3 required about 250 cc.

It was found almost impossible to get white precipitates after igniting, this being especially true where the new magnesia mixtures were used. Reigniting, after adding a few drops of nitric acid, changed the precipitates to grayish white, and lowered the weights 0.3 of a milligram (average of nine determinations).

The precipitates from the new magnesia mixtures were very fine, and exhibited a marked tendency toward going through the filters of Gooch crucibles.

C. L. Sargent, Rhode Island.—The “white precipitates” were washed with about 100 cc of wash solution, and were practically free from chlorids. The precipitates were black in every case where the official magnesia mixture was used, and with magnesia mixtures Nos. 1 and 2 the precipitates from samples 1 and 2 were black and from No. 3 gray; 20 cc of official magnesia mixture were used for sample No. 1, 10 cc for No. 2, and 15 cc for No. 3.

R. G. Newborne, North Carolina.—The magnesium ammonium phosphate precipitates were burned to whiteness.

F. B. Carpenter, North Carolina.—The “white precipitates” were washed practically free of chlorids, which required from 200 cc to 250 cc of wash solution. They were also burned to whiteness.

William Allen, North Carolina.—My “white precipitates” were washed practically free of chlorids and were burned to whiteness.

Reporter.—All my “white precipitates” were washed practically free of chlorids

and burned to whiteness. I find no difficulty in burning precipitates to whiteness or to a grayish white, at least when they have been previously washed free of chlorids and dried before burning.

C. L. Hare, Alabama.—My "white precipitates" were washed free of chlorids and burned to a light gray, no further loss taking place on burning to whiteness.

ADDITIONAL RESULTS FOR COMPARISON OF MAGNESIA MIXTURE NO. 2 WITH
OFFICIAL MAGNESIA MIXTURE.

Mr. John P. Street, of the New Jersey Station, has made determinations of total phosphoric acid in ninety-six fertilizers, using magnesia mixture No. 2 in comparison with the official one. Mr. Street comments as follows upon his results:

I have given the new magnesia mixture (No. 2) a thorough test, and am very much pleased with it. I found from my results on the official samples that mixture No. 2 gave the better results; probably there is too much citric acid in No. 1. I therefore used No. 2 throughout in my comparative work. The saving of time by this new mixture is large, and it seems to me that more uniformity is obtained. The adoption of this modification would mean a great deal to us, as it requires considerable time to add the old magnesia mixture drop by drop. I also send some results where I used the new mixture in duplicate determinations. Their close agreement shows the uniformity of results obtained with the new mixture. Seven of the ninety-six samples gave wide results, varying from 0.28 to 0.38 per cent higher by the new method. In my judgment this apparent discrepancy was not in any way due to the methods, but owing to the fact that all of the analyses were made in the rush of routine work, and lack of time had prevented the necessary repetition of the work. They are therefore omitted from the averages, which are 10.94 for the official method and 10.96 for the new magnesia mixture.

TABLE II.—Comparative results on total phosphoric acid by the official magnesia mixture and magnesia mixture No. 2.

[John P. Street, analyst.]

No. of sample.	Official mag-nesia mix-ture.	New mag-nesia mix-ture No. 2.	No. of sample.	Official mag-nesia mix-ture.	New mag-nesia mix-ture No. 2.	No. of sample.	Official mag-nesia mix-ture.	New mag-nesia mix-ture No. 2.	No. of sample.	Official mag-nesia mix-ture.	New mag-nesia mix-ture No. 2.
	<i>Per ct.</i>	<i>Per ct.</i>		<i>Per ct.</i>	<i>Per ct.</i>		<i>Per ct.</i>	<i>Per ct.</i>		<i>Per ct.</i>	<i>Per ct.</i>
337	10.53	10.64	361	7.54	7.63	385	9.99	10.28	410	14.26	14.36
338	7.09	7.11	362	11.78	11.91	386	11.50	11.55	411	12.57	12.48
339	12.14	12.45	363	11.78	11.90	387	9.41	9.49	412	11.53	11.63
340	12.67	12.80	364	12.04	12.07	388	14.02	14.02	413	10.18	10.18
341	13.86	13.86	365	8.41	8.47	389	9.35	9.47	414	11.77	11.77
342	14.82	14.95	366	10.95	10.93	390	8.27	8.61	415	11.67	11.74
343	11.96	12.10	367	8.69	8.55	391	9.37	9.75	416	12.94	13.06
344	8.93	9.05	368	10.81	10.90	392	12.47	12.52	417	9.30	9.40
345	9.61	9.70	369	12.78	12.89	393	10.21	10.30	418	10.73	10.63
346	6.77	6.91	370	8.36	8.36	394	12.18	12.18	419	13.06	13.06
347	9.60	9.64	371	9.54	9.60	395	9.40	9.67	420	12.25	12.15
348	10.14	10.14	372	11.00	11.08	396	8.03	7.93	421	11.26	11.17
349	13.39	13.51	373	13.01	12.90	397	11.93	12.04	422	9.21	9.09
350	13.36	13.21	374	11.21	11.35	398	11.03	11.09	423	9.53	9.41
351	13.61	13.73	375	9.58	9.52	399	9.54	9.64	424	9.53	9.49
352	12.38	12.28	376	10.76	10.78	400	12.53	12.40	425	12.95	12.83
353	12.05	12.03	377	8.78	8.89	401	11.80	12.08	426	9.06	9.11
354	11.04	11.05	378	10.65	10.52	402	9.49	9.61	427	11.88	11.83
355	12.99	12.89	379	9.75	9.75	403	9.70	9.82	428	14.06	14.06
356	10.47	10.40	380	9.15	9.30	404	10.21	10.32	429	9.12	8.98
357	10.94	10.94	381	11.00	10.90	405	10.65	10.96	430	12.26	12.26
358	8.61	8.61	382	13.40	13.47	406	7.67	7.73	431	11.87	11.85
359	12.31	12.41	383	12.78	12.68	407	8.06	8.13	432	12.39	12.27
360	11.12	11.09	384	12.81	12.67	408	8.72	8.80	433	9.42	9.40
Average.....									10.94	10.96

DISCUSSION OF RESULTS.

Gravimetric method, official magnesia mixture.—Phosphate solution No. 1 sent out contained 10 grams c. p. disodiumhydrogen phosphate (Na_2HPO_4 , 12 H_2O) to the liter, the theoretical percentage of P_2O_5 in this salt being 19.826. The highest result obtained on this sample was 20.50 per cent and the lowest 19.75 per cent, the former being 0.674 of 1 per cent above the theory and the latter but 0.076 of 1 per cent below the theory. The average of all results is 20.044 per cent, which is 0.218 of 1 per cent above the theoretical content, and the variation between highest and lowest results is 0.75 of 1 per cent. Fourteen per cent of the determinations were within 0.05 of 1 per cent of the theory; $33\frac{1}{3}$ per cent within 0.10 of 1 per cent, and $55\frac{1}{2}$ per cent within 0.2 of 1 per cent. On the whole, these results make a slightly better showing toward accuracy than did those of last year on the same phosphate, but like the results of last year most of them are high. Last year there were two results below the theory, 19.74 and 19.78; this year there are also two below, 19.75 and 19.78, the lowest of the former being 0.08 of 1 per cent below the theory and of the latter 0.07 of 1 per cent. Last year the result highest above the theory was 0.84 of 1 per cent and this year 0.76 of 1 per cent.

Phosphate solution No. 2 was No. 1 diluted with five parts of water, and therefore contained 3.304 per cent of P_2O_5 . The highest result obtained on this sample was 3.65 per cent, or 0.346 of 1 per cent above the theory; and the lowest result was 3.20 per cent, which is 0.104 of 1 per cent below the theory. Out of forty-two results on this sample, there are four below the theory, these variations being 0.10, 0.02, 0.02, and 0.01 of 1 per cent, while the greatest variation above the theory is 0.346 of 1 per cent. Sample No. 3 was a mixed fertilizer, and we do not therefore know its exact content of phosphoric acid. The average and variations from this are given for what they are worth, which is very little. Judging, however, from the work on the other samples of c. p. phosphates, I would say that the content of phosphoric acid in this sample is not far from 12.40 per cent. This would indicate that most of the results on this sample are also too high.

All this adds to the point dwelt upon at considerable length in my report on this subject last year, that our official method for phosphoric acid gives high results in the hands of nearly all, if not all, workers, and may give extremely high ones in the hands of some. We have the consolation, however, of knowing (as the reporter sees it) that there is no well-established method of sufficient rapidity that suits our needs better or with which we can get better results.

New magnesia mixtures Nos. 1 and 2.—These need not be discussed at any length. The reporter admits that his afterwork (after sending out the instructions) with them has not been satisfactory. While the average results with them on all the samples are much nearer the theory than those obtained with the official mixture, the variations are quite wide. In some hands they have given high results, and in others low ones, while in others still the results have been perfectly satisfactory, this latter being especially true of Mr. Street's results. Mr. Street has done more work with them than anyone else, and his results deserve special mention. Of the two new magnesia mixtures, No. 1, as would be expected, generally gave the lower results on account of the larger amount of citric acid contained in it.

The new magnesia mixtures were in practically 2.5 per cent ammonia solution, and the ammonium phosphomolybdate was also dissolved in 2.5 per cent ammonia. The object of the reporter in directing in the instructions that the mixtures be added at once with stirring was on the ground that in this way an excess of both ammonia and magnesium chlorid would be present before precipitation commenced, and hence no monomagnesium diammonium phosphate, as claimed by von Lorenz, would form, and the presence of citric acid would prevent the formation of trimagnesium phosphate, so there would only form magnesium ammonium phosphate. On this supposition, were the precipitation complete, the results would be correct. It would seem, therefore, that the reporter did not strike the proper conditions for

obtaining correct results by the use of citric acid, if it be true, as stated by Von Lorenz, that citric can be used in this way for getting theoretical results by the molybdate method. F. Bergami, in a recent article,¹ shows that to get results by the citrate method that are comparable with those by the molybdate method, the amount of citrate solution used must be carefully regulated, and Dr. Johnson, in the article already referred to, states that the conditions under which the citrate method will give good results "must be empirically determined." It is therefore probable that should the proper conditions be found for using citric acid in the way it has been used in the investigation of this year, good would then be obtained.

II.—RESULTS ON REPORTER'S SAMPLE NO. 3 BY THE CITRATE METHOD.

Dr. Fassbender, of Kempen a -Rh., reports as follows:

Sample No. 3:	Per cent.
Total phosphoric acid.....	{ 12.45
	{ 12.61
Citrate-soluble phosphoric acid	{ 8.15
	{ 8.17

Total phosphoric acid was determined by the method given by Dr. Fassbender last year, and the citrate-soluble by the method of Wagner² as given for basic slag.

Dr. Wernskiold, of the Christiania Chemical Control Station of Norway, reports on sample No. 3:

	Per cent.
Total phosphoric acid	12.56
Water-soluble phosphoric acid	7.98
Soluble in alkaline ammonium citrate	2.30
Insoluble	2.28

Total was determined by the citrate method, and the phosphoric acid soluble in alkaline ammonium citrate was determined according to the method³ of Direks and Wernskiold.

Mr. E. G. Runyan, of the United States Department of Agriculture, reports total P_2O_5 in No. 3 by the German citrate method, as follows: 12.82, 12.91, 12.50, and 13.10 per cent (average, 12.83 per cent), the average of his results by our official method being 12.53 per cent, or 0.30 of 1 per cent lower than by the German citrate method. He also reports citrate-soluble in No. 3, determined by the method described by Runyan and Wiley⁴, as follows: 2.29, 2.49, and 2.08 per cent, the official method, by difference, giving him 3.40 per cent.

III.—VOLUMETRIC DETERMINATION OF PHOSPHORIC ACID.

While the results by the volumetric method last year were encouraging, they were not such as to give the analysts who tried it any considerable faith in it as it then stood, especially for high percentages, and some considered it without advantage over the gravimetric method, and unreliable. With these views of the method in the minds of the analysts, the reporter feared that it would be a waste of time to again send out the method for investigation without making some improvement in it. The reporter accordingly spent at least a month in the spring, before sending out samples, in the study of the method in its various phases and in trying numerous modifications.

The results obtained by the reporter, and presented in a paper⁵ to this association

¹ Jour. Franklin Inst., August, 1895.

² Wiley's Agr. Anal., II, pp. 7, 79.

³ Landw. Versstat., XXXIV, p. 425.

⁴ Jour. Am. Chem. Soc. XVII, 513.

⁵ Bul. 43, U. S. Dept. Agr., Div. Chem., p. 100.

last year, by a different method of precipitation and washing, were much more uniform and satisfactory than those obtained by the original Pemberton method. This modified method gave quite as good results in the reporter's hands as did the official method. It was therefore decided to use 60° C. as the temperature of precipitation and the official molybdate, instead of boiling temperature and the aqueous molybdate, as used by Pemberton, as the starting point for the investigation.

Knowing that molybdic acid was the cause of the trouble in the volumetric method, various ways of getting rid of it were tried. After several failures, an attempt was made to find wash solutions which would dissolve molybdic acid, but not ammonium phosphomolybdate.

Using a c. p. disodium hydrogen phosphate solution (= 19.826 per cent P_2O_5), the following results were obtained with different strengths of nitric acid for washing, finishing with potassium nitrate solution and water to remove nitric acid.

Wash solutions.

Number of times washed with H_2O by decantation.	Number of times washed with dilute HNO_3 by decantation.	Number of times washed with 3 per cent KNO_3 by decantation.	Washed on filter with H_2O cc.	5 cc 1.42 sp. gr. HNO_3 in 100 cc water.	10 cc 1.42 sp. gr. HNO_3 in 100 cc water.	20 cc 1.42 sp. gr. HNO_3 in 100cc water.	Washed with water only.
				<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
.....	1	2	275	19.80
1	1	1	275	19.84
2	1	275	19.98
.....	2	1	400	19.80
.....	2	1	400	19.87
1	2	275	19.80
3	400	19.98
.....	2	1	230	19.87
.....	2	1	350	19.83
3	700	19.93
3	550	19.85

The washing with dilute nitric acid and 3 per cent potassium nitrate was always by decantation, using 50 cc to 75 cc, agitating thoroughly, and allowing the precipitate to completely settle each time.

SOLUBILITY OF MOLYBDIC ACID IN VARIOUS WASH SOLUTIONS.

The next point investigated was the solubility of molybdic acid in various solutions which might be used for washing. This solubility is expressed in terms of the number of cc of the standard alkali used in the volumetric method, neutralized by the molybdic acid dissolved; 100 cc of this alkali is equal to 32.38 cc of normal alkali.

Solubility of MoO_3 in various wash solutions.

No. of MoO_3 used.	Amount of MoO_3 used.	Amount of solutions.	Time of standing.	Water.	2 cc 1.42 sp. gr. HNO_3 in 100 cc H_2O .	5 cc 1.42 sp. gr. HNO_3 in 100 cc water.	10 cc 1.42 sp. gr. HNO_3 in 100 cc water.	20 cc 1.42 sp. gr. HNO_3 in 100 cc water.	2.5 per cent KNO_3 .	5 per cent KNO_3 .	5 per cent NaNO_3 .
		cc.	hrs.	cc alk.	cc alk.	cc alk.	cc alk.	cc alk.	cc alk.	cc alk.	cc alk.
1	2	100	1	11.4	-----	-----	5.6	6.8	20.4	20.5	20.5
2	1	100	2	-----	7.4	8.1	8.8	-----	-----	2.75	-----
3	1	100	$\frac{1}{2}$	-----	21.3	1.5	$\left. \begin{array}{l} 32.8 \\ 20.2-2.3 \end{array} \right\}$	2.8	3 per cent KNO_3 20.9	-----	-----
				2.45	.8	1.5				.25	-----
				-----	22.4	23.55				2.95	-----
4	1	100	1	-----	22.9	24.7	7.3	8.85	21.0	-----	-----
				$\frac{1}{2}$	41.4	-----	$\left. \begin{array}{l} 2.2 \\ 2.2 \end{array} \right\}$	-----	.8	-----	-----
5	1	100	1	-----	-----	-----	2.8	-----	.7	-----	-----
				-----	-----	-----	2.8	-----	.8	-----	-----
				-----	-----	-----	2.8	-----	.8	-----	-----

¹ Stood eighteen hours and then filtered turbid, though double filter was used; result too high.

² Filtered turbid; results too high.

³ Used as in washing the "yellow precipitate"—one portion of 100 cc was added, stirred, and allowed to stand fifteen minutes and filtered off, when another portion of 100 cc was added and treated in the same way.

⁴ Stood twenty-four hours before clear filtrate could be obtained.

These solubility determinations were made by allowing 100 cc of the respective solutions to stand in a beaker with the molybdic acid for the times indicated in the table, stirring once or twice to keep the molybdic acid in contact with the liquid, but allowing sufficient time before filtration for most of it to settle to the bottom of the beaker. The washes were then filtered through double filters, evaporated to dryness (where nitric acid was present), heated in air bath till nitric acid was driven off, and titrated. It was found very difficult to prevent the molybdic acid from passing through the filter when water was used as the solvent. It would remain suspended in very finely divided state in water for twenty-four hours and pass through the filter. The results for the water solubility are therefore generally too high. This is also true to a less extent of the solubility in 2.5, 3, and 5 per cent potassium nitrate solutions, and in the 5 per cent sodium nitrate solution, and to a still less extent of the solubility in 2 and 5 cc of nitric acid solutions.

The results are not all uniform, but fairly so when the same molybdic acids were used. None of these molybdic acids were pure. Nos. 1 and 2 contained considerable quantities of ammonium nitrate and molybdate of ammonia, and perhaps some sodium molybdate. Nos. 3, 4, and 5 were washed by decantation for a day or more with large quantities of dilute nitric acid, and finally with water once or twice, and contained, so far as we ascertained, only molybdates as impurities. These impurities did not, we think, materially affect the solubility of these acids in the wash solutions. The results, at any rate, are of value in showing the comparative solvent action of the different washes for molybdic acid under conditions similar to those in which they are used in the method.

They show that water and the potassium and sodium nitrate solutions have very little solvent action, while that of the stronger nitric acid solutions is quite considerable.

The dilute nitric acid wash containing 10 cc of 1.42 sp. gr. nitric acid in 100 cc of the wash was adopted for washing because it possesses good solvent power for molybdic acid, and is of practically the same acidity as the solution in which the

precipitation of phosphomolybdate of ammonium is made in the official method. The official molybdic solution contains nearly 15 cc of 1.42 sp. gr. nitric acid in 50 cc, and a solution requiring 50 cc of molybdic solution to precipitate the phosphoric acid in it usually has a volume near 100 cc; the two would give a volume of 150 cc, containing about 10 cc nitric acid in the 100 cc. We know that precipitation is complete in a solution of this acidity, and no solvent action takes place even on long standing. It therefore seems reasonable to conclude that nitric acid of the same strength would exert little or no solvent action on the ammonium phosphomolybdate in the short time required to wash the precipitate.

SOLUBILITY OF PHOSPHOMOLYBDATE OF AMMONIA IN THE FOREGOING WASH SOLUTIONS.

It now seemed necessary to investigate the solubility of ammonium phosphomolybdate in these same wash solutions. This was done by preparing a pure phosphomolybdate of ammonia from sodium phosphate by precipitating with a deficient quantity of molybdic solution. This ammonium phosphomolybdate contained 3.789 per cent P_2O_5 , the theory being 3.783, showing that it was practically pure. The solubility is expressed in terms of the number of cc of standard volumetric alkali required to neutralize the phosphomolybdate dissolved; 1 cc of this alkali equals 1 milligram P_2O_5 .

Solubility of ammonium phosphomolybdate in wash solutions.

	Amount of solution.	Time of standing.	Water at 65°.	Water at laboratory temperature, about 27° C.	2 cc HNO_3 in 100 cc of wash.	5 cc HNO_3 in 100 cc of wash.	10 cc HNO_3 in 100 cc of wash at 65° C.	10 cc HNO_3 in 100 cc of wash at laboratory temperature.	20 cc HNO_3 in 100 cc of wash.	3 per cent KNO_3 .
	cc.	hrs.	cc alk.	cc alk.	cc alk.	cc alk.	cc alk.	cc alk.	cc alk.	cc alk.
0.75 to 1.4 grams stood in 500 cc of the solutions for the times indicated and 200 cc taken therefrom each time.	200	24	15.2	10.85	0.2	0.25	20.1	0.6	0.75	0.5
	200	106	26.0	33.0	2.05	5.5	216.75	6.75	11.45	4.35
Results from allowing precipitates from 20 per cent phosphate to stand in those solutions.	200	$\frac{1}{2}$	None.	None.	None.	None.	None.
	200	1	Trace.	Trace.	Trace.	Trace.	Trace.

¹These filtered very turbid; they had not settled in twenty-four hours, and the precipitate ran through.

²These stood at laboratory temperature (about 27°) after the first twenty-four hours.

³Filtered turbid; result too high.

From 0.75 to 1.4 grams of the prepared phosphomolybdate was shaken up in flasks with 500 cc of the wash solutions; 200 cc of this was filtered off at the end of twenty-four and one hundred and six hours, respectively, evaporated to dryness, the nitric driven off, and the residue titrated. The phosphomolybdate settled in only two or three of those washes in less time than twenty-four hours, and even then the very fine particles remained suspended in the water solutions, and it was found impossible to get clear filtrates from them. The results for water solubility are therefore too high. For the reason just stated the solubility of ammonium phosphomolybdate in the washes could not be determined for the times they would ordinarily stand in contact with the precipitate in washing by the use of the pure molybdate. If, however, the solubility of even this pure phosphomolybdate was proportional to the time of standing in the washes the amount that would have been

dissolved by all the washes (dilute nitric acid, potassium nitrate, and water) used in washing a precipitate in the ordinary thirty minutes required for washing could hardly have been found. I calculate that on this basis a plus correction of about 0.016 of 1 per cent would be necessary on basis of 0.2 gram substance.

The solubility of the "yellow precipitate," just as it is precipitated in ordinary work along with the salts carried down with it, was also determined in the wash solutions by allowing 200 cc of them to stand in contact with the precipitate for one-half and one hour, respectively, after stirring thoroughly. The precipitates settle completely and quickly in this way. In none of these washes could more than a trace of phosphoric acid be found.

Again, all the washings (3,600 cc) from six determinations of phosphoric acid in samples 1 and 2, sent out by the reporter, were combined, evaporated down, and the phosphoric acid in them determined by the gravimetric method, when 0.38 milligram P_2O_5 was found corresponding to a plus correction of 0.03 of 1 per cent on 0.2 gram basis.

A similar result was obtained from the washings from eight determinations in samples 1 and 2. These results indicate that while the wash solutions used in the work on the volumetric methods this year have marked solvent power for molybdic acid, they have practically no solvent action on phosphomolybdate of ammonia, and that a correction for ordinary work at least is not necessary. There is danger, however, from mechanical loss. The precipitate is first washed by decantation with dilute nitric acid and potassium nitrate, and afterwards with water to remove the nitric acid. In this after washing, when all the salts have been removed from the precipitate and as much as 600 or 700 cc of water have been used, the precipitate begins to pass through the filter mechanically and settle to the bottom of the receptacle. I do not, however, and most of the analysts this year have not found it necessary, to wash with more than 300 cc of water. I consider that 500 or 600 cc may be used without this loss, but the filtrate should be closely observed when it goes beyond this amount.

COMMENTS OF ANALYSTS UPON THE DETERMINATION OF PHOSPHORIC ACID BY THE VOLUMETRIC METHOD.

H. C. Sherman, Maryland.—My work with the volumetric method has been mainly on low percentages; 300 to 400 cc of water was usually sufficient for washing the precipitates free of acid. The results are perfectly satisfactory, agreeing well with those obtained by the official method, though generally a little lower. When the reporter's instructions about precipitation were followed, no trouble was experienced in the subsequent filtration and washing. The only objection of importance to the method is the bluish color in titration, which sometimes interferes with the end reaction, but this does not occur in low percentages. I used 2-inch funnels with platinum cones and filter paper for filtering, employing suction.

F. P. Veitch, Maryland.—Filtration was made in the Gooch crucible, with two pieces of filter paper slightly larger than the bottom of the crucible pressed tightly against the bottom with a stirring rod. It was found necessary to cut the paper slightly larger than the bottom of the crucible to prevent the precipitate from running through. Using this filter, I washed twice with dilute nitric acid and once with potassium nitrate by decantation, as directed by the reporter; then twice by decantation, with about 25 cc of water each time. The precipitate was then brought upon the filter, the beaker washed out twice, the crucible removed from the receiver and washed on the outside, and the inside of the rubber holding the crucible was washed; the crucible was replaced and the precipitate washed several times with water, using suction and allowing each portion of wash to run through before adding more. By this method of washing, 200 cc of water was sufficient to free precipitate of acid, and no blue color was developed in the titration to interfere with the end reaction. The method worked well with me, my results being good.

W. A. Powers, Illinois.—Used the Gooch crucible for filtering in the volumetric method.

Maurice Bird, Louisiana.—Used Swedish filter paper for filtering in the volumetric method.

R. G. Newborne, North Carolina.—Used the Hirsch funnel for filtering in the volumetric method.

W. M. Allen, North Carolina.—While a student of the University of North Carolina I made several determinations of phosphoric acid by the volumetric method, but was unable to free the phosphomolybdate precipitate from molybdic acid by washing with water, and my results were consequently too high as well as not concordant; but by washing as directed by the reporter this difficulty has been entirely obviated in my practice with the method as sent out for investigation this year.

I ran six determinations at a time, precipitated at 65° , in water bath, allowed to stand six minutes after the molybdic solution was added, and filtration was completed in two and one-half minutes after taking out of bath. It required about thirty minutes to wash six precipitates with the dilute nitric acid, potassium nitrate solution, and water. My results by the method have been good, and I am very much pleased with it.

F. B. Carpenter, North Carolina.—In my work on the volumetric method the instructions were followed as closely as possible with the exception of the time of precipitation, which was extended to six minutes, and the temperature ranged from 62° to 65° during precipitation. Precipitation at 65° is quicker and does not seem to affect the results, and I would regard this as perhaps the best temperature to use in this method.

My experience with the volumetric method as sent out this year has been very satisfactory. Everything considered, I believe it will prove more desirable than the present gravimetric method. The work can be carried on with much greater rapidity and the results are more uniform than by the gravimetric method.

C. B. Williams, North Carolina.—I have made about two hundred and fifty determinations of phosphoric acid by the volumetric method as sent out by the reporter this year, and have found the precipitation, filtration, and washing to be perfectly satisfactory. The neutral point in titration can be easily determined after a little practice. On chemically pure phosphates this method has given me almost theoretical results, while the official gravimetric method gave almost invariably high results. I consider the volumetric method better than the gravimetric, not only in that it gives more accurate results, but also in that at least twice as many determinations can be made by it as by the gravimetric.

R. E. Noble, Alabama.—My results by the volumetric method as sent out by you this year agree well with those by the official method, though slightly lower and more uniform. The present method is free from the criticism of excessive and objectionable washing necessary in the Pemberton method. In fact, I have found 250 cc of water to be sufficient in all cases to free the precipitate from acid, and most of them were freed with 175 to 200 cc. I do not consider it necessary to test to see if all acid is removed when as much as 250 cc of wash water has followed the decantation washings with dilute nitric acid and potassium nitrate, but titrate at once with perfect safety. The method saves time, and is an improvement in every way over the official one.

C. L. Hare, Alabama.—Used glass funnels, platinum cones, and asbestos for filtering; washed with 250 to 350 cc of water, and considers the volumetric method, when manipulated with the necessary care, more reliable than the present gravimetric one.

RESULTS OBTAINED BY THE VOLUMETRIC METHOD.

The results obtained on the samples sent out by the reporter by the volumetric method are brought together in Table III, beside the official gravimetric results of the same analysts. The gravimetric results here are a portion of those presented in Table I for the comparison of magnesia mixtures. Some of the higher gravimetric results, however, do not appear here, and hence the average is lower than in Table I, but the discussion of the gravimetric results given there also applies here.

TABLE III.—Total P_2O_5 by gravimetric and volumetric methods, reporter's samples.

Analyst.	No. 1. Methods and washing.				No. 2. Methods and washing.				No. 3. Methods and washing.			
	Official gravimetric.	Volumetric.	Washings, water.	Difference (+) greater (—) less than gravimetric.	Official gravimetric.	Volumetric.	Washings, water.	Difference (+) greater (—) less than gravimetric.	Official gravimetric.	Volumetric.	Washings, water.	Difference (+) greater (—) less than gravimetric.
	<i>Perct.</i>	<i>Perct.</i>	<i>cc.</i>	<i>Perct.</i>	<i>Pr. ct.</i>	<i>Pr. ct.</i>	<i>cc.</i>	<i>Perct.</i>	<i>Perct.</i>	<i>Perct.</i>	<i>cc.</i>	<i>Perct.</i>
H. C. Sherman and F. B. Bomberger, Maryland Agricultural College.	20.09	19.82	400	— .194	3.43	3.35	400	— .09	12.54	12.55	300	— .07
	19.98	19.93	350		3.38	3.30	390		12.61	12.57	360	
	20.05	19.79	330		3.42	3.32	320		12.65	12.47	300	
F. P. Veitch, Maryland Agricultural College.	20.10	19.83	100	— .335	3.47	3.20	175	— .245	12.65	12.28	275	— .375
	20.23	3.25	175		12.70	12.37	150	
	12.25	90	
H. C. Sherman, Maryland Agricultural College.	— .02	12.48	12.50	650
		12.51	12.45	300	
	
Maurice Bird, Louisiana Experiment Station.	20.39	20.16	500	— .235	3.45	3.37	500	— .07
	20.45	20.21	500		3.41	3.35	500		
	
R. G. Newborne, North Carolina Agricultural College.	19.87	19.74	500	— .194	3.22	3.25	500	— .024	12.15
	20.07	19.73	400		3.38	3.30	400		12.28	
	19.86	500		3.28	500		
W. A. Powers, Illinois Experiment Station.	19.91	3.65	12.27	12.30	500	— .06
	19.92		3.49		12.35	12.20	500	
	19.85		3.47	
E. G. Runyan, United States Department of Agriculture.	19.83	19.81	550	+ .037	3.28	3.33	450	— .01	12.29	12.45	600	+ .06
	19.77	19.81	530		3.28	3.33	725		12.48	12.50	525	
	19.75	19.84	550		3.45	3.28	510		12.53	12.50	550	
W. M. Allen, North Carolina Experiment Station.	19.93	19.81	275	— .11	3.38	3.28	265	— .109	12.50	12.32	275	— .178
	19.97	19.84	250		3.39	3.27	300		12.59	12.39	300	
	19.96	19.88	285		3.27	275		12.39	350	
C. B. Williams, North Carolina Experiment Station.	19.91	19.80	220	— .073	3.32	210	12.32	240
	19.85	230		3.32	220		12.32	270	
	19.85	250		3.32	205		12.32	235	
F. B. Carpenter, North Carolina Agricultural Experiment Station.	19.83	19.85	275	+ .03	3.38	3.32	250	— .006	12.43	12.39	250	+ .01
	19.87	275		3.33	3.34	250		12.37	12.43	250	
	
B. W. Kilgore, North Carolina Experiment Station.	19.96	19.83	280	— .12	3.38	3.32	300	— .083	12.40	225
	19.89	19.83	280		3.39	3.31	200		12.40	190	
	20.00	19.83	250		3.40	3.30	200		12.37	200	
Not included in averages:	3.30	210	12.37	250
R. E. Noble, Alabama Experiment Station.	19.91	19.85	3.35	3.35	12.51	12.40
	19.92	19.85	250	3.33	3.37	250	12.46	12.40
	19.89	19.85	3.43	3.35	12.52	12.40	250

TABLE III.—Total P_2O_5 by gravimetric and volumetric methods, etc.—Continued.

Analyst.	No. 1. Methods and washings.				No. 2. Methods and washing.				No. 3. Methods and washing.			
	Official gravimetric.	Volumetric.	Washings, water.	Difference (+) greater (-) less than gravimetric.	Official gravimetric.	Volumetric.	Washings, water.	Difference (+) greater (-) less than gravimetric.	Official gravimetric.	Volumetric.	Washings, water.	Difference (+) greater (-) less than gravimetric.
Not included in averages.—Continued.	<i>Per ct.</i>	<i>Per ct.</i>	<i>cc.</i>	<i>Per ct.</i>	<i>Pr. ct.</i>	<i>Pr. ct.</i>	<i>cc.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>cc.</i>	<i>Per ct.</i>
C. L. Hare, Alabama Experiment Station.	20.02	19.74	3.39	3.33	12.90
B. B. Ross, Alabama Experiment Station.	20.00	19.62	250	3.33	3.30	250	12.85
Average	19.79
Theory	19.98	19.84	3.39	3.310	12.47	12.40
Variation of lowest result from theory.	19.826	19.826	3.304	3.304
Variation of highest result from theory.	.076	.126084	.104
	.624	.384346	.066

The volumetric results are what I deem may be termed most excellent. The theoretical percentage of phosphoric acid in phosphate solution No. 1 is 19.826, and the average of all results by the volumetric method is 19.84, or 0.014 of 1 per cent above the theory; 73 per cent of all the results are within 0.05 of 1 per cent of the theory, and 93 per cent within one-tenth of 1 per cent of the theory, there being only three results varying more than one-tenth. Phosphate solution No. 2 contained 3.304 per cent P_2O_5 and the average of all results is 3.301, or 0.006 of 1 per cent below the theory; 85 per cent of the results are within 0.05 of 1 per cent of the theory, and all are within one-tenth. Considering that this is the first time the majority of the analysts have used the method, the results are very gratifying.

The results of last year by the volumetric method as originally described by Pemberton, and as modified by the reporter, were considered as only encouraging. It may not therefore be out of place here to ask, Why this sudden change from encouraging or indifferent results to extremely good ones? The reporter feels that he has answered this question in the foregoing outline he has given of his investigation of the method during the past nine months, and would sum up his reasons for the change as consisting in (1) a different temperature of precipitation, (2) a different molybdc solution, and (3) different manner of washing and wash solutions. In his own hands the reporter considers that the volumetric method will give more accurate results than the official gravimetric method; his three coworkers look upon the method in the same light, and most of those who have worked with it this year seem to share the same opinion. Besides, a man can turn out from two to three times as much work by the volumetric as by the gravimetric method.

ADDITIONAL RESULTS BY THE VOLUMETRIC METHOD.

In Table IV are presented quite an array of results on various materials (164) comparing the volumetric with the gravimetric method. With a few exceptions the results are good. This, I may say, is invariably the case with low and medium percentages. With the high percentage materials, however, there are a number of rather wide variations, the lower results with two exceptions being by the volumetric method. When we observe the close agreement of the results on the same sample

by the volumetric method, and remember the tendency of the gravimetric method to give high results, we are strongly inclined to accept the volumetric results as being nearer the truth.

TABLE IV.—*Determinations of phosphoric acid in various materials by gravimetric and volumetric methods.*

[H. C. Sherman and F. P. Veitch, analysts, Maryland Agricultural College, College Park, Md.]

Material.	Number.	Gravimetric method.	Volumetric method.	Washings, water.	Difference (+) greater (-) less than gravi- metric method.	Material.	Number.	Gravimetric method.	Volumetric method.	Washings, water.	Difference (+) greater (-) less than gravi- metric method.
		Per ct.	P. ct.	cc.	P. ct.			Per ct.	P. ct.	cc.	P. ct.
Insolubles in reg- ular fertilizer						Insolubles in reg- ular fertilizer					
work	1	3.49	3.58	+ .09	work	42	3.34	3.25	— .09
Do.....	2	1.70	1.67	— .03	Do.....	43	1.97	1.96	— .01
Do.....	3	1.82	1.67	— .15	Do.....	44	.96	.88	— .08
Do.....	4	.96	.90	— .06	Do.....	45	2.58	2.45	— .13
Do.....	5	4.74	4.59	— .15	Do.....	46	3.91	3.87	— .04
Do.....	6	2.61	2.51	— .10	Do.....	47	3.25	3.20	— .05
Do.....	7	1.12	1.05	— .07	Do.....	48	1.07	1.00	— .07
Do.....	8	2.24	2.18	— .06	Do.....	49	1.50	1.41	— .09
Do.....	9	.64	.67	+ .03	Do.....	50	2.85	2.71	— .14
Do.....	10	1.28	1.29	+ .01	Do.....	51	1.17	1.18	+ .01
Do.....	11	1.33	1.46	+ .13	Do.....	52	2.69	2.68	— .01
Do.....	12	2.51	2.58	+ .07	Do.....	53	5.46	5.43	— .03
Do.....	13	1.84	1.72	— .12	Do.....	54	2.80	2.69	— .11
Do.....	14	1.06	1.03	— .03	Do.....	55	1.36	1.29	— .07
Do.....	15	1.25	1.15	— .10	Do.....	56	.70	.68	— .02
Do.....	16	.96	.93	— .03	Do.....	57	1.39	1.49	+ .10
Do.....	17	1.60	1.66	+ .06	Do.....	58	3.02	3.03	+ .01
Do.....	18	2.05	2.01	— .04	Do.....	59	.83	.90	+ .07
Do.....	19	3.30	3.33	+ .03	Do.....	60	.82	.97	+ .15
Do.....	20	2.35	2.43	+ .08	Do.....	61	2.16	2.14	— .02
Do.....	21	1.81	1.77	— .04	Do.....	62	.94	1.07	+ .13
Do.....	22	4.56	4.45	— .11	Do.....	63	2.00	2.04	+ .04
Do.....	23	1.39	1.32	— .07	Do.....	64	1.78	1.64	— .14
Do.....	24	2.82	2.70	— .12	Do.....	65	.74	.80	+ .06
Do.....	25	1.46	1.34	— .12	Do.....	66	.24	.30	+ .16
Do.....	26	.30	.33	+ .03	Do.....	67	1.28	1.38	+ .10
Do.....	27	2.40	2.4000	Do.....	68	2.03	2.09	+ .06
Do.....	28	2.43	2.30	— .13	Do.....	69	.96	1.08	+ .12
Do.....	29	.46	.40	— .06	Do.....	70	2.21	2.11	— .10
Do.....	30	2.91	2.95	+ .04	Do.....	71	1.98	1.99	+ .01
Do.....	31	2.96	3.00	+ .04	Do.....	72	1.41	1.56	+ .15
Do.....	32	2.83	2.78	— .05	Do.....	73	1.60	1.56	— .04
Do.....	33	3.08	3.05	— .03	Do.....	74	1.60	1.46	— .14
Do.....	34	2.54	2.52	— .02	Do.....	75	1.54	1.5400
Do.....	35	.66	.6600	Do.....	76	2.18	2.20	+ .02
Do.....	36	1.36	1.38	+ .02	Do.....	77	.83	.90	+ .07
Do.....	37	1.79	1.7900	Do.....	78	2.21	2.09	— .12
Do.....	38	1.50	1.56	+ .06	Do.....	79	3.81	3.79	— .02
Do.....	39	1.38	1.45	+ .07	Do.....	80	1.33	1.37	— .04
Do.....	40	1.65	1.51	— .14						
Do.....	41	.50	.5000	Average dif- ference.....					— .02

TABLE IV.—*Determinations of phosphoric acid in various materials by gravimetric and volumetric methods—Continued.*

[H. C. Sherman, analyst, Maryland Agricultural College.]

Material.	Number.	Gravimetric method.	Volumetric method.	Washings, water.	Difference (+) greater (-) less than gravi- metric method.	Material.	Number.	Gravimetric method.	Volumetric method.	Washings, water.	Difference (+) greater (-) less than gravi- metric method.
		<i>Per ct.</i>	<i>P. ct.</i>	<i>cc.</i>	<i>P. ct.</i>			<i>Per ct.</i>	<i>P. ct.</i>	<i>cc.</i>	<i>P. ct.</i>
Mixed fertilizer ...	1	1.41	1.39	200	— .02	Peruvian guano...	8	3.30	3.18	— .12
Do.....	2	2.64	2.59	— .05	Do.....	9	1.46	1.39	— .07
Do.....	3	3.20	3.13	— .07	Acid phosphate...	10	.83	.80	— .03
Do.....	4	2.83	2.76	— .07	Do.....	11	1.26	1.16	— .10
Do.....	5	2.82	2.81	— .01	Dissolved bone ...	12	1.93	1.89	— .09
Do.....	6	3.36	3.26	— .10	Average dif-					
Do.....	7	3.01	2.96	— .05	ference.....					— .07

[F. C. Veitch, analyst, Maryland Agricultural College.]

Reporter's sample No. 2 for 1894, gravimetric aver- age 17.31 per cent.	1	17.48	17.20	130	— .28	Reporter's sample No. 3 for 1894, theory 19.826 (!) per cent	2	19.88	100
Reporter's sample No. 1 for 1893, average 13.03 per cent	3	13.33	12.79	138	— .54	Laboratory sample	4	15.38	15.20	150	— .18
Laboratory sample.	6	7.15	7.15	125	.00	Do.....	5	10.54	10.45	80	— .09
Do.....	8	14.90	14.60	150	— .30	Do.....	7	21.12	20.66	110	— .46
Florida phosphate.	10	38.44	37.38	275	—1.06	Reporter's sample No. 2 for 1893, average 36.30 per cent	9	26.26	35.89	190	— .37

¹ C. p. Na₂HPO₄. 12 H₂O = 19.826 per cent P₂O₅.

[E. G. Runyan, analyst, United States Department of Agriculture.]

Laboratory sample.	1	19.78	19.70	575	— .08	Laboratory sample.	6	30.82	30.25	510	— .57
Do.....	2	1.34	1.35	520	— .01	Do.....	7	14.10	14.80	450	+ .70
Do.....	3	19.46	19.30	550	— .16	Do.....	8	16.81	16.90	450	+ .09
Do.....	4	6.00	5.80	525	— .20	Do.....	9	17.29	17.30	425	— .01
Do.....	5	10.14	10.12	550	— .02	Do.....	10	15.57	15.55	550	— .02

[C. B. Williams, analyst, North Carolina Experiment Station.]

Cotton-seed meal ..	1	.08	.08	130	.00	Fertilizers and fer- tilizing materials	15	10.04	10.05	220	+ .01
Fertilizers and fer- tilizing materials.	2	.27	.35	160	— .02	Do.....	16	9.54	9.45	260	— .09
Do.....	3	1.32	1.28	100	— .04	Do.....	17	10.72	10.65	270	+ .07
Do.....	4	1.50	1.45	240	— .05	Do.....	18	6.46	6.40	230	— .06
Do.....	5	.88	.79	215	— .09	Do.....	19	6.55	6.60	250	+ .05
Do.....	6	.65	.61	250	— .04	Do.....	20	5.45	5.50	290	— .05
Do.....	7	.64	.61	250	— .03	Do.....	21	6.52	6.60	280	.08
Do.....	8	1.27	1.25	240	— .02	Do.....	22	7.47	7.44	230	+ .03
Do.....	9	1.29	1.25	250	— .04	Do.....	23	7.42	7.48	230	+ .04
Do.....	10	4.96	4.95	155	— .01	Do.....	24	17.55	17.52	260	— .03
Do.....	11	4.98	4.92	180	— .06	Florida phosphate.	25	38.12	37.84	260	— .28
Do.....	12	11.80	11.80	120	.00	Acid phosphate...	26	15.49	15.35	290	— .14
Do.....	13	11.58	11.45	250	— .13	Do.....	27	13.27	13.15	280	— .12
Do.....	14	9.77	9.80	240	+ .03						

TABLE IV.—*Determinations of phosphoric acid in various materials by gravimetric and volumetric methods—Continued.*

[W. M. Allen, analyst, North Carolina Agricultural Experiment Station.]

Material.	Number.	Gravimetric method.	Volumetric method.	Washings, water.	Difference (+) greater (-) less than gravi- metric method.	Material.	Number.	Gravimetric method.	Volumetric method.	Washings, water.	Difference (+) greater (-) less than gravi- metric method.
		<i>Per ct.</i>	<i>P. ct.</i>	<i>cc.</i>	<i>P. ct.</i>			<i>Per ct.</i>	<i>P. ct.</i>	<i>cc.</i>	<i>P. ct.</i>
Mixed fertilizer....	1	11.58	11.49	263	-.09	Acid phosphate...	3	15.49	15.45	260	-.04
Do	2	9.54	9.52	280	-.02	Mixed fertilizer...	4	10.72	10.69	270	-.03

[B. W. Kilgore, analyst, North Carolina Experiment Station.]

Mixed fertilizer....	1	9.77	9.76	275	-.01	Mixed fertilizer...	11	10.72	10.68	275	-.04
Do	2	9.03	8.96	210	-.07	Acid phosphate...	12	13.27	13.21	275	-.06
Do	3	10.67	10.66	220	-.01	Mixed fertilizer...	13	11.71	11.63	275	-.08
Do	4	11.58	11.60	275	+.02	Do	14	11.88	11.75	275	-.13
Do	5	9.77	9.76	275	-.01	Do	15	9.43	9.38	250	-.05
Do	6	10.04	10.01	275	-.03	Do	16	9.71	9.80	230	+.09
Do	7	9.54	9.48	275	-.06	Bone meal.....	17	10.38	10.30	250	-.08
Acid phosphate....	8	15.49	15.42	275	-.07	Acid phosphate...	18	20.53	20.48	210	-.05
Insoluble	9	2.57	2.60	230	+.03	Do	19	15.02	15.10	220	+.08
Reporter's sample No. 1 ¹	10	19.89	19.88	260	-.01	Reporter's sam- ple No. 2 ²	20	3.39	3.31	220	-.08

¹ C. p. Na_2HPO_4 , 12 H_2O = 19.826 per cent P_2O_5 .² Theory 3.304 per cent P_2O_5 .

RESULTS ON A HIGH-GRADE FLORIDA PHOSPHATE.

A solution of a high-grade Florida phosphate was made by the reporter, a portion of which was sent to Mr. F. P. Veitch, of the Maryland Agricultural College, for analysis, and the remainder kept for analysis by the reporter and Mr. C. B. Williams of the North Carolina Experiment Station. Results as follows were attained:

Method.	Veitch.	Williams.	Kilgore.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
Volumetric.....	37.38	37.80	37.80
	37.38	37.84	37.88
	37.38
Gravimetric.....	38.44
	38.44	38.12
Difference, less by volumetric.....	1.06	.30

IV.—CITRATE-SOLUBLE, INSOLUBLE, AND SOLUBLE PHOSPHORIC ACID.

The results for citrate-soluble phosphoric acid by the direct method of Ross and by the official method of difference are too few to warrant much discussion, and no conclusion can be drawn from them. The results for insoluble and soluble are also few in number, and amount to little more than a comparison of the volumetric and gravimetric methods in the determination of these forms of phosphoric acid. All these results are presented in Table V.

TABLE V.—*Citrate-soluble, insoluble, and soluble phosphoric acid, reporter's samples.*

Analyst.	Citrate-soluble phosphoric acid.			Insoluble phosphoric acid, sample No. 3.			Soluble phosphoric acid, sample No. 3.		
	Found after treating by Ross method.	Found after evaporating and igniting.	Citrate-soluble by difference.	Gravimetric method.	Volumetric method.	Difference.	Gravimetric method.	Volumetric method.	Difference (+) greater (—) less than gravimetric.
E. G. Runyan, United States Department of Agriculture:	<i>Mgr.</i>	<i>Mgr.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>
Phosphate solution No. 1, 10 cc = 19.826 milligrams P_2O_5 added.	19.52	20.29
	19.71	20.35
	<i>Per ct.</i>	<i>Per ct.</i>							
Mixed fertilizer No. 3	3.05	3.18	3.38	1.30	1.33	{+.02	7.85
	3.11	3.25	3.40	1.28	1.30		7.85
C. B. Williams, North Carolina Experiment Station:	<i>Mgr.</i>								
Phosphate solution No. 1, 10 cc = 19.826 milligrams P_2O_5 added.	20.28
	20.14
	<i>Per ct.</i>								
Mixed fertilizer No. 3	3.10	3.08	3.52	1.27	1.25	{-.03	7.47	7.44	0.00
	3.58	3.13	3.50	1.29	1.25		7.42	7.44	
	3.22	7.44	
	3.40	7.48	
F. B. Carpenter, North Carolina Experiment Station: Mixed fertilizer No. 3.	1.28	1.22	{-.03	7.69	7.60	-.10
	1.25	1.24		7.58	
	1.25	7.60	
	7.60	
W. A. Powers, Illinois Experiment Station: Sample No. 3.	1.20	
	1.22	
	1.22	
H. C. Sherman and F. B. Bomberger, Maryland Agricultural College: Sample No. 3.	1.51	1.57	+.03	
	1.48	1.55		
	1.50	1.45		
H. E. Curtis, Kentucky Experiment Station:									
Sample No. 3	4.26	3.59	3.39	1.46	7.64	
10 cc phosphate solution No. 1	17.86	20.28	
C. L. Hare, Alabama Experiment Station: Sample No. 3.	3.23	1.52	8.13	
B. B. Ross, Alabama Experiment Station: Sample No. 3.	3.41	3.47	3.26	

¹ Contained impurity.

WASHING AND BURNING THE MAGNESIUM AMMONIUM PHOSPHATE PRECIPITATE.

The reporter begs to again bring to the attention of the association the questions of washing and burning the "white precipitate." Some, in reply to these questions sent out by the reporter, state that they wash with 100 cc of wash solution, while others use as much as 250 to 300 cc. All the methods for determining phosphoric acid as magnesium ammonium phosphate, so far as I am aware, require that this precipitate shall be washed free of chlorids. We consider that our method should require this also.

As regards burning, some analysts state that they have found it impossible to get white precipitates, even after moistening with nitric acid and reigniting, while others report having burned to whiteness without difficulty. The reporter has never had difficulty in burning to whiteness, or to a grayish white at least, when the precipitates have previously been washed free of chlorids and dried. First importance should be attached to getting a pure precipitate, and secondly to getting it into the crucible in a dry, powdery condition. When paper is used for filtering and it is attempted to burn heavy precipitates, collected in this way, wet, they form a lump or lumps, and it is almost impossible to burn them white—on the inside at any rate.

MAKING NEUTRAL CITRATE OF AMMONIA.

The reporter also makes mention of the procedure which has been followed in the New Jersey Station for six or more years, and to which De Roode¹ called attention, for making neutral ammonium citrate.

RECOMMENDATIONS.

(1) That the directions given in Bulletin 43 (Chem. Div. U. S. Dept. Agr., p. 342), second to last line in last paragraph under "Total phosphoric acid," for washing and burning the magnesium ammonium phosphate precipitate, be made to read: Filter, wash with 2.5 per cent NH_3 solution until free of chlorids, ignite to whiteness or to a grayish white, and weigh.

(2) That the volumetric method, as investigated this year, be made an alternate method for phosphoric-acid determination.

ESTIMATION OF PHOSPHORIC ACID IN SOILS BY DOUBLE PRECIPITATION WITH MOLYBDIC SOLUTION AND TITRATION OF THE AMMONIUM PHOSPHOMOLYBDATE WITH STANDARD ALKALI

By C. B. WILLIAMS.

The accurate estimation of the small quantities of phosphoric acid usually present in the acid extract of soils is a question that has given no small amount of trouble in soil analysis. There seems to be two main difficulties: First, in the precipitation with molybdic solution in the presence of large quantities of iron and aluminium salts. Compounds of these latter elements are also often precipitated with the ammonium phosphomolybdate, and are either dissolved by the ammonia wash or remain in the cone of the filter as phosphates, thus giving rise to high or low results, as the case may be, unless special precautions are taken. In the second place, very small quantities of phosphoric acid are not precipitated readily by magnesium chlorid mixture and usually require long standing to be complete, in which case the precipitate is very liable to contain an excess of magnesia, thus giving rise to high results.

Some work in the laboratory of the North Carolina Experiment Station upon the samples sent out by Prof. A. M. Peter, reporter on soils, indicates that these difficulties are readily overcome by the following procedure: After the soil extracts have been obtained as directed by Professor Peter, and care has been taken to get rid of all organic matter, in the hydrochloric acid extract as well as in the organic acid extracts, portions of the organic acid solutions corresponding to 18 to 20 grams of the soil and to 1 or more grams of the hydrochloric acid solution (according to the amount of phosphoric acid present) are precipitated, after adding about 15 grams ammonium nitrate, at 40° with a large excess of molybdic solution (30 cc is usually enough), let stand four hours, filter, and wash with water twice. Now dissolve the precipitate into the beaker used for precipitation with dilute ammonia, wash the filter with dilute nitric and add concentrated nitric acid until precipitate begins to reform; add 10 grams ammonium nitrate, digest in water bath at

¹ Jour. Am. Chem. Soc., XVII, 47.

65°, add 2 cc strong nitric acid with vigorous stirring, let stand five minutes, add 2 cc molybdic solution, let stand eight minutes more, and filter, wash, and titrate according to volumetric method used in this laboratory.¹

The results presented in the following table were obtained in the course of this investigation and show very close agreement with each other on the same solutions.

Volumetric determination of phosphoric acid in soils by double precipitation with molybdic solution—first, at 40° in water bath with 30 cc of official molybdic solution; second, at 65° in water bath with concentrated nitric acid and 2 cc of molybdic solution—compared with official gravimetric method.

Sample—	Hydrochloric acid solution.			Citric acid solution.		Oxalic acid solution.
	Official gravimetric method.	First solution.	Second solution.	First solution.	Second solution.	Second solution.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
No. 1.....	0.4505	0.4170	0.4069	0.0282	0.0290	0.0505
		.4170	.4069	.0282	.0287	.0505
		.4170	.4069	.0282	.0287	.0510
		.4170	.4069	.0282	.0287	.0510
No. 2.....	.1720	.1826	.1826	.0119	.0146	.0060
		.1775	.1826	.0119	.0146	.0060
		.1826	.1928	.0119	.0146	.0065
		.1826	.1928	.0122	.0152	.0065
No. 3.....	.3956	.3767	.3867	.0233	.0255	.0475
		.3869	.3867	.0233	.0255	.0475
		.3869	.3867	.0233	.0255	.0483
		.3767	.3818	.0233	.0261	.0483
		.3767
		.3818
No. 4.....	.1932	.1828	.1929	.01570087
		.1878	.1929	.01570087
		.1928	.1929	.01570087
		.1878	.1878	.01620084

REPORT ON THE INVESTIGATIONS OF METHODS FOR PHOSPHORIC ACID DETERMINATION FOR THE A. O. A. C. FOR 1894.

By E. SOLBERG,

Assistant chemist of the Chemical Control Station of Christiania, Norway.

For want of time, we have not carried out the work in the detailed manner we had hoped to do. Our work falls into two divisions:

I. Determination of phosphoric acid according to the methods generally used by us.

II. According to the official methods of the A. O. A. C.

I.—DESCRIPTION OF METHOD—TOTAL PHOSPHORIC ACID.

For determining total phosphoric acid in bone-meal, fish, guano, etc., and superphosphate, 5 grams of the substance are boiled half an hour with 20 cc 1.42 sp. gr. nitric and 50 cc 1.8 sp. gr. sulphuric acid in a 500 cc flask, diluted with water, and,

¹See description of volumetric method by reporter on phosphoric acid in this Bulletin.

after cooling, made up to the mark; 50 cc of the filtrate is made alkaline with ammonia, then acid with nitric acid, precipitated with 50 cc molybdic solution for every 0.1 gram P_2O_5 present, heated in water bath for one hour, and allowed to stand twelve hours more, when the filtrate is decanted, the precipitate washed thoroughly with dilute molybdate water (1 to 4), dissolved in warm dilute ammonia, and the filter washed out with hot water. The ammoniacal solution is neutralized with hydrochloric acid, cooled, mixed drop by drop, with constant stirring, with 10 to 20 cc magnesia mixture, and after a quarter of an hour one-third the volume of 10 per cent ammonia is added. This is allowed to stand two hours, is filtered, washed with 5 per cent ammonia until the disappearance of the chlorin reaction, dried, burned in open crucible over a Bunsen flame, and finally, for a quarter of an hour, in covered crucible heated to glowing over the blast lamp.

WATER-SOLUBLE PHOSPHORIC ACID.

To 20 grams substance in a liter flask is added 800 cc water, and agitated every fifteen minutes during two hours; it is now made up to the mark, and the phosphoric acid in 50 cc of the filtrate, equaling 1 gram substance, determined as under total.

REVERTED (CITRATE-SOLUBLE) PHOSPHORIC ACID.

The method of Direks and Wernskiold (Landw. Versuchst., XXXIV) was used; 2.5 grams substance are rubbed up with water, then washed onto the filter with about 100 cc water, the residue sprayed with a part of the measured-off (below) citrate solution, and digested one hour at 35° to 40° with 200 cc of Petermann's citrate solution. The water and citrate extracts are made up to 250 cc, and the phosphoric acid determined in 25 to 50 cc, according to the richness in phosphoric acid. [This would give the available (water-soluble and citrate-soluble) phosphoric acid. The reverted is doubtless determined in the citrate extract alone, or by difference as in our method.—REPORTER.]

NOTE.—The German citrate method is also used by us in our work, but for various reasons it could not be employed in this investigation.

Molybdate solution.—Three hundred and seventy-five grams molybdate of ammonia are dissolved in 2.5 liters of water and the solution poured into 2.5 liters of nitric acid of sp. gr. 1.20.

Magnesia mixture.—Two hundred and seventy-five grams crystallized chlorid of magnesium and 350 grams chlorid of ammonium are dissolved in 3,250 cc of water and filled up to 5 liters with ammonia of sp. gr. 0.96.

Petermann's solution.—One kilogram citric acid is dissolved in about 2 liters of water and 1,350 cc of ammonia of sp. gr. 0.925, and filled up with water to 5,750 cc. The solution then has a sp. gr. of 1.09; 300 cc of ammonia of sp. gr. 0.925 are now added.

II.—DETERMINATION OF PHOSPHORIC ACID ACCORDING TO THE A. O. A. C. METHODS— TOTAL PHOSPHORIC ACID.

For the solution of acid phosphate No. 2 and superphosphate No. 336, official method No. 4 was used; while for castor pomace and cotton-seed meal and fish guano, methods 1 and 3 were employed. Method No. 1 seems to have given too low results on fish guano.

Total and water-soluble phosphoric acid in reporter's and other samples as determined by different methods, by E. Solberg, of the Christiania Chemical Control Station of Norway.

	Total phosphoric acid.								Water-soluble phosphoric acid.			
	I. Method used at the Christiania Station.		II. Official method of the A. O. A. C.						I. Method as used at the Christiania Station.		II. Official method of the A. O. A. C.	
			(1) Mg (NO ₃) ₂ .	(4) HNO ₃ and HCl.	(3) H ₂ SO ₄ .							
No. 1. Castor pomace and cotton-seed meal.....	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.
	2.61	2.65	2.56	2.59	2.53	2.56	0.71	0.74
No. 2. Acid phosphate...	17.40	17.41	17.41	17.38	12.08	12.07	12.13	12.19
No. 3. Phosphate solution	20.65	20.67	20.62	20.62
No. 336. Superphosphate	11.85	11.84	11.84	11.84	10.08	10.08	9.92	9.94
No. 375. Fish guano.....	14.21	14.18	14.04	14.08	14.23	14.21

Citrate-soluble and insoluble phosphoric acid as determined by different methods, by E. Solberg.

	Citrate-soluble phosphoric acid.								Insoluble phosphoric acid.			
	I. Dircks and Wernskiold's method.		II. Official method.		Dircks and Ross's method.		Reporter's method for insoluble.		II. Official ignition method.		II. Reporter's modification of direct solution in HNO ₃ and HCl.	
No. 1. Castor pomace and cotton-seed meal.....	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.
	1.64	1.64	1.60	1.61	1.73	1.71	0.19	0.20	0.10	0.13
No. 2. Acid phosphate...	1.31	1.32	1.78	1.80	1.79	1.84	1.63	1.63	3.45	3.42	3.59	3.60
No. 336. Superphosphate	1.24	1.26	1.53	1.52	1.51	1.54	1.47	1.51	.38	.39	.44	.40

Remarks of E. Solberg.—In boiling the two superphosphate samples with sulphuric acid, very strong spattering occurred and the reaction did not proceed smoothly, but if boiled a little before adding the sulphuric acid the spattering was entirely avoided. We always wash the magnesium ammonium phosphate precipitate completely free of chlorids, which usually requires 150 to 200 cc ammonia wash. [He uses 5 per cent ammonia.—REPORTER.]

Dr. F. D. Wernskiold, director of the Chemical Control Station of Norway, in a letter to the reporter, after expressing regret at not being able, owing to the pressure of other duties, to carry out the comparative work in the comprehensive manner at first intended, makes the following remarks on the American methods:

Permit me to make some remarks concerning the American methods, if I may do so without giving offense.

In my opinion, for Norwegian, Swedish, Danish, and German conditions, the American methods in question for the determination of phosphoric acid are—notwithstanding their analytical exactness—quite inapplicable. With us, many, in part, poorly pulverized and badly mixed manures, such as ammonium superphosphate, potassium superphosphate, and potash-ammonio superphosphate, are employed, and these can not usually be so well pulverized and mixed that one can take out a true sample of 2 or 2.5 grams for analysis for the greatest exactness and conscientiousness; and care in the analysis is useless when the material employed does not represent the average condition of the materials used in the mixtures. We therefore use for the preparation of the solutions to be examined, only very unwillingly, less than 10 or 20 grams and almost never less than 5 grams of substance, unless we are obliged to—as, for instance, in the determination of nitrogen and reverted phosphoric acid.

[The foregoing report was mailed to me first on July 14, 1894, but owing to incorrect address it was returned to Christiania and remailed. For this reason it did not reach me in time to be included in my report to the association in 1894.—REPORTER.]

GOSS METHOD FOR TOTAL ACID-SOLUBLE PHOSPHORIC ACID.

In the case of ordinary soils, weigh out 10 grams of the sifted air-dried sample, transfer to a pear-shaped straight-necked Bohemian glass digesting flask which has been marked to hold 250 cc, and add approximately seven-tenths gram of yellow oxid of mercury and 20 to 30 cc of concentrated sulphuric acid, as for the determination of nitrogen. Twenty cc of acid are usually sufficient, but in the case of very finely divided clay soils containing little or no sand it is necessary to use 30 cc to prevent caking of contents of flask. In doubtful cases 20 cc of acid should first be added, and at the end of five or ten minutes, if contents show a tendency to cake, 10 cc more should be introduced. Thoroughly mix contents of flask by shaking, place on a suitable support over a burner, boil for one hour, cool (cold water can not safely be used), add about 100 cc of water, 5 cc of concentrated hydrochloric acid, and 2 cc of concentrated nitric acid, heat to boiling to oxidize iron, cool (cold water can safely be used), make up to volume, and filter through a dry folded paper until perfectly clear. In order to secure a clear filtrate, it will usually be found necessary to pour the first portion of the filtrate back through the paper three or four times. Transfer 100 cc of the filtrate to an ordinary flask of about 450 cc capacity, add strong ammonia until a permanent precipitate forms, then 6 or 8 cc of nitric acid to dissolve the precipitate, and boil until clear. Cool the solution to 85°, add 75 cc of recently prepared molybdate solution, place the unstoppered flask, for fifteen minutes, in an open water bath kept at 80°, shake flask vigorously four or five times while in the bath, then remove and let stand ten minutes to allow the precipitate to settle. Filter through a 9 cm. No. 589 S. and S. filter, avoiding too strong pressure at first; wash the flask and precipitate thoroughly with 10 per cent ammonium nitrate solution acidified with nitric acid; place the flask in which the precipitation was made under the funnel, shut off pump and close all valves to filtering jar to form an air cushion and prevent too rapid filtration; fill paper one-half full of hot water, add a few cubic centimeters of strong ammonia, and aid solution if necessary by stirring the precipitate with a small glass rod. As soon as the yellow precipitate is dissolved, open valve to filtering jar, but do not turn on the pump; after the solution has all passed through, rinse paper once with a small amount of hot water; after the last portion has passed through, remove flask and place a small lipped beaker under the funnel, heat solution in flask to boiling, and again pour through the paper, avoiding the use of the pump at first, as otherwise loss from spattering is likely to ensue. It is a good plan to have the beaker covered with a perforated watch glass, through which the funnel passes. Finally, wash out the flask and paper with a small amount of hot water (the total filtrate should not exceed 50 cc).

As has been pointed out by Hilgard, aluminum is sometimes carried down with the phosphoric acid from soil solution upon precipitating with molybdate solution, in which case some of the phosphoric acid will not be dissolved in the treatment with ammonia. This will be indicated, first, by the appearance of a white precipitate upon dissolving the yellow precipitate in ammonia, and, second, by the difficulty experienced afterwards in washing. If such a precipitate be present in any appreciable quantity, proceed as follows: After washing out all the ammoniacal solution as directed above, place a small beaker under the funnel, close all valves, fill the filter one-third full of hot water, add the same amount of concentrated hydrochloric acid, proceed as if dissolving phosphomolybdate in ammonia, receiving final solution and washing in the flask previously used; dilute with water to about 100 cc, add 20 cc of 75 per cent ammonium nitrate solution, neutralize with ammonia, clear up solution with nitric acid, precipitate with 50 cc of molybdate solution in exactly the same manner as before, filter off precipitate, wash, dissolve in ammonia, and add to first portion.

To the warm ammoniacal solution in the beaker add hydrochloric acid until the yellow color appears, then add a few drops of ammonia until the solution clears; cool, add 5 cc of filtered magnesia mixture from a burette, drop at a time, with constant stirring; let stand fifteen minutes, add 20 cc of strong ammonia, sp. gr. 0.9, allow to stand over night, filter, wash precipitate with dilute ammonia, dry, ignite intensely over blast lamp for ten minutes, cool in a desiccator, and weigh the $Mg_2P_2O_7$ secured.

The reagents used, which have not already been described, are the same as used in the official fertilizer work.

For a detailed discussion of this method see A. O. A. C. report for 1894, page 58.

No further papers being presented, the discussion of the report was declared to be in order.

Mr. HUSTON. I would like to suggest to the reporter that as complete an analysis of sample No. 3 as is practicable be given in the report. Very often I find, in looking back over our old reports, that when we want to figure some on them we are met with the difficulty that there is no complete analysis, nor are the soluble, the reverted, and the insoluble phosphoric acid always given in discussing some of the samples. I think it would be well to have a complete statement of the composition of these products, because sometimes we want to go further than the reporter, and it takes but a few minutes to insert the figures.

Mr. Kilgore stated that he had all of the results in his report, and that he gave the soluble, citrate-soluble, and insoluble phosphoric acid in the table by the method of Ross. He said there were very few results, and he combined them in one table. Only four or five men gave results on soluble or reverted phosphoric acid.

Mr. Huston stated that the greatest variation seemed to be in the Florida phosphate, and he thought as complete information as might be had should be given concerning its composition; the iron, alumina, etc., he thought would at some time become of considerable interest. By giving as many figures as could be obtained, they might be of considerable help to some one who might consider the matter later on.

Mr. Kilgore said he took the matter up at the last meeting. He had obtained something like 85 per cent phosphate of lime in a sample collected by himself, and which he knew to be high grade.

Mr. Wheeler called attention to the fact that criticisms had been made by official chemists and others in regard to the variations in results on phosphoric acid. In some cases the insoluble and soluble would decrease and the reverted would increase; in others the soluble would increase and the reverted would decrease without any particular change in the insoluble. He thought it might be well to specify that the insoluble acid should be determined on one day by all the chemists taking part in the work, so that changes in the reverted acid would be exactly alike.

Mr. Huston said it was formerly the custom to make determinations on the same day, but attention has been diverted by the determinations, and the details lost sight of.

Mr. Ross. I would like to say a few words in regard to the citrate-

soluble matter. Last year a comparison of the results by the citrate method was made with the results by difference. It was stated at that time that in the washing process of the citrate method a considerable amount, or at least an appreciable amount, of phosphoric acid was always washed out by the wash water after filtration. This year we decided it would be best to send out a sample of chemically pure phosphate and try this method, and also to take a portion of the filtrate, evaporate it, treat it with magnesium nitrate, and ignite, so as to compare the results obtained with the phosphoric acid actually known to be present. Compare these results on this basis, and it seems some results are not very bad. With the mixed fertilizer No. 3, the results by one analyst by the citrate method were 3.5 and 3.11; by igniting with magnesium nitrate, 3.19, 3.35. The next set of results by the method that I recommended, 3.10, 3.22, 3.40, 3.58; by magnesium nitrate, 3.08, 3.18. At the same time the results by difference are 3.52, 3.50. In our own laboratory some results obtained direct by citrate-soluble were 3.39, 3.43; magnesium nitrate, 3.45, 3.49; citrate-soluble by difference, 3.26. Now, these are all the results that have been given. I consider the variation in the results obtained by the method which bears my name small as compared with those obtained by the magnesium nitrate method.

Mr. Ross then gave some figures obtained in the examination of a sample of chemically pure phosphate, and concluded by saying that on the basis of a comparison with the phosphoric acid actually known to be present he thought there were no great discrepancies.

Mr. Kilgore said that he did not make an official report on the Ross method; he merely commented on the fact that the results were too few to report.

Mr. HUSTON. I have been considerably interested in the report on phosphoric acid, and I note one expression recurring in regard to chemically pure phosphate. We are investigating all raw materials used in the manufacture of fertilizers in my laboratory on a pretty elaborate scale, and it is unnecessary to say that we have not got very far yet. I wish it were possible to utilize some volumetric method, as it would be an important matter with us in making so many determinations. My assistant and myself decided that if we could check a volumetric method against a chemically pure phosphate it would be of value. We started for the chemically pure phosphate. We have not found it yet, although we went over the whole list. Phosphate of soda we found to be condemned in all sorts of terms as being largely contaminated with carbonic acid, lime, water of crystallization, and as generally unreliable. Then we abandoned phosphate of soda and went through the whole list of phosphates. The only two which seemed to promise anything at all were phosphate of silver and phosphate of zinc. The zinc salt was absolutely nothing at all. It was neither one salt nor the other, nor a definite mixture of two. We have not been able to get

a normal phosphate of silver. We are still hoping that the next sample will be better, but so far we have not succeeded in finding a chemically pure phosphate. In the group of pyrophosphates we were met at the outset with the same trouble. In regard to the precipitation of molybdic acid in connection with the yellow precipitate, it may be that we will find a promising solution in a sulphuric-acid solution of molybdic acid—that is, molybdic solution made up with sulphuric acid. The only acid present, then, is sulphuric. The process works very well so far as I can see, and gives good results as compared with the other methods. The molybdic solution prepared with sulphuric acid is extremely permanent. We have some which has been made up for two years, and which shows no trace of a residue on treatment with nitric acid.

The work which I simply want to outline briefly, not to present in the form of a paper, consists in taking the raw materials of the fertilizer trade and determining the action of ammonium citrate upon them: First, the time element; second, the temperature element; third, the quantity element; fourth, acid, and fifth, alkaline citrate. The quantity element is quite an important one in a great deal of work, particularly with calcium salts. [Mr. Huston here exhibited a chart showing the results of some work done in his laboratory, and illustrating the importance of the time, temperature, quantity, acid, and alkali elements.]

Mr. WHEELER. Have you tried this on iron and alumina phosphates?

Mr. HUSTON. Yes.

Mr. WHEELER. In working with these materials, do you reduce them all to a uniform state of fineness?

Mr. HUSTON. Yes; we try to. We can get the same state of fineness that we get with calcium phosphates. Steamed bone is giving us a good deal of trouble. It is difficult to get consistent results with this material. We are now working with a machine, and it does better work. I want the members of the association to know what the results of this work are, and will be glad to explain at any time.

Mr. WINTON. Are you working with any other solution than ammonium citrate?

Mr. HUSTON. We have not, so far.

Mr. PERSONS. Would it not be in order now to say something in regard to the estimation of iron and alumina in natural phosphates? In our laboratory in Florida we have always found a great deal of trouble in getting a satisfactory method for the estimation of iron and alumina; the method we have considered most satisfactory there has been the removal of the molybdenum from the filtrate from the phosphomolybdate precipitate by hydrogen sulphid. I prefer it to the Glaser method. The great trouble with the precipitation of the molybdenum is getting rid of it before precipitating the iron and alumina. In order to do this, the solution from the phosphomolybdate has to be diluted to a larger volume, and then the hydrogen sulphid gas passed through. I

suppose something like a liter is necessary for precipitation. Under these circumstances, it always takes us at least a day to get all the molybdenum precipitated out, and then we have to evaporate the filtrate to a small volume before precipitating the iron and alumina. I have been working to find some method that would effect this result with more rapidity. I believe I am on the track of one now that will solve the problem. I don't claim it is perfect, having given it only a few weeks' examination. I have obtained some good results with it, though since I left Florida my assistant has written me that his results have not been so favorable. The scheme that we have in view there is based upon the removal of the molybdenum with nascent hydrogen sulphid, and it is done without diluting the filtrate from the phosphomolybdate precipitate to any large volume. The plan we are following and hope to work out is, we take this phosphomolybdate precipitate or filtrate and first neutralize it with ammonia. To this solution we add ammonium polysulphid. This precipitates the iron as sulphid and leaves the alumina as hydroxid. We add to this filtrate hydrochloric acid to effect the solution of the iron and alumina, convert the iron into chlorid, and thus liberate hydrogen sulphid. I found I got almost perfect precipitates inside of five minutes. After precipitating the molybdenum and bringing the iron and alumina back into solution as chlorids, we filter, leaving the molybdenum on the filter paper, and the iron and alumina in solution. Wash the precipitate thoroughly with hydrogen sulphid, add the solution containing iron and alumina, and precipitate with ammonia to get a precipitate of iron and alumina. Possibly a little iron may go down with the molybdenum. I think by redissolving with hydrochloric acid, and reprecipitating, that can be removed, and I believe if the association would work along this line we could get a method more rapid and more accurate than the methods we are now accustomed to use. The question of the determination of iron and alumina is equally important with phosphoric acid, so far as getting accurate results. If we can get out a method along these lines, I believe it will be of service to the association.

Mr. HUSTON. There is no question about the desirability of determining iron and alumina in phosphates. I have been running down a few methods this year and no two of them are alike in my hands, and my results range from 6 per cent to 16.5 per cent. I think the Girard tin method is really the best one I have tried. The results were constant and the precipitate appeared to be pure. The question has come before the association, but very few have worked upon it. Samples have not been distributed for the determination of iron and alumina, except one in 1891. There is no question in regard to the importance of the matter, especially to those who have to deal with natural phosphates. I am inclined to believe the question of the determination of iron and alumina will assume greater importance in the future.

Mr. PERSONS. I neglected to say that before precipitating the iron

and alumina in the last stage you have to boil and expel the hydrogen sulphid before adding ammonia.

Mr. HUSTON. There is an electrolytic method of getting it out. Simply take molybdic acid, put in a platinum dish, and run an electric current through it. It is a good idea to evaporate the whole then to dryness in the first place to get rid of a good deal of ammonium nitrate in that sort of material.

Mr. BIGELOW. It appears to me that thioacetic acid might work very well for removing the molybdenum. I saw some experiments last week, by Dr. T. H. Norton, at the Springfield meeting of the American Association for the Advancement of Science. He was giving a number of experiments before the association which had been outlined by Schiff and Tarugi. It is well known that thioacetic acid was originally suggested to replace hydrogen sulphid in the laboratory primarily on account of the unpleasant odor which we associate with hydrogen sulphid. I was disappointed to find, however, that the odor of thioacetic acid is certainly as objectionable, and by many is considered more objectionable, than that of hydrogen sulphid.

Mr. DAVIDSON. Four years ago the subject was talked of a good deal, and Mr. Wilkinson suggested to the association a method of removing iron and alumina without precipitating molybdenum at all. Favorable results were obtained by precipitating the solution in the cold, allowing it to stand for several hours, and treating with hydrochloric acid.

Mr. KILGORE. I would like to again refer to the insoluble and citrate-soluble method of Ross. We have found this year that after treating the insoluble residue with the citrate solution it continued to dissolve or wash through the filter. I should like to have Mr. Ross modify his method so it would give good results.

Mr. ROSS. I would like to modify it so that others could get as good results as I do.

Mr. WHEELER. I understand that some members of the association wash after treating with ammonium citrate on filter paper, and others use a Gooch crucible. Some wash with suction, others without. Owing to the difficulty that chemists of the association have in making their results check with commercial chemists, I am of the opinion that allowing the filtration to go on so slowly is possibly in order that the operation may be continued as long as possible. Commercial chemists try in every possible way to get around the directions of our association, so as to get as much of available acid as possible.

Mr. HUSTON. I have the same difficulty; but allowing it to remain doesn't make high available, but high insoluble. It depends upon what the material is.

Mr. ROSS here exhibited to the members of the association a mechanical stirrer. He said that where a large amount of phosphoric acid work was done it was necessary to employ some more expeditious and less tedious method of stirring than by the hand.

Mr. HUSTON remarked that the question of stirrers was an important one in his work.

Mr. HUSTON. I would like to suspend any further discussion now to get the reports of some of the committees before the association. I would like to get the recommendations of the reporters in order that the committees may have opportunity to work on them.

Mr. KILGORE. With reference to the sodium phosphate I sent out, I considered, from all the evidence that I could get, that it was a chemically pure phosphate. It had been carefully preserved, and in appearance the crystallization was perfect. I analyzed it very carefully by the volumetric method, and the results corresponded with the theoretical percentages, dissolving the precipitate and reprecipitating in alcohol to get rid of the excess of magnesia, and these results agreed with others. This work was done by three men.

Mr. HUSTON then asked Mr. Kilgore to read the recommendations of the reporter on phosphoric acid.

Mr. Kilgore asked for a little time.

Mr. KILGORE. I merely make a suggestion in regard to the neutralization of the citrate by dissolving in ammonia and allowing to stand until it becomes neutral, which requires about half a day, or by allowing it to stand over night. We would like to use the volumetric method in our laboratory. We are perfectly satisfied with it. We have been using it a good deal. The results have been checked against the gravimetric method, and we have gotten better results with the volumetric. They are slightly lower and more concordant. I consider the method perfectly safe. At the same time I recognize that not many chemists have been working on it, only about three or four stations exercising fertilizer control. I will say that it gave the best set of results, even if it is the first time the method has been used, that I have ever seen given before the association. I don't like to be premature or see a method put in among the official methods and then thrown out. I recommend that it be made a provisional method used for checking.

Mr. HUSTON. We have next in order the report of the abstract committee. Perhaps we can take that up before dinner.

Mr. FREAR. In accordance with the instructions of the association at the last meeting, I conferred with the Assistant Secretary of Agriculture and Professor True, director of the Office of Experiment Stations, and made an arrangement by which the abstracts could be published promptly in the Experiment Station Record. There had been some delay in the matter, but it was finally settled, and a circular letter was sent to the members of the committee. After a very considerable delay, unanimous consent had been received to the plan proposed.

The next step was to secure cooperation, and this I found difficult. I finally, however, succeeded in securing the pledge of some half dozen upon specific work. Some of them have, in accordance with the arrangement, reported material promptly to the director of the Office of Experi-

ment Stations, and these abstracts have appeared. I must confess that your chairman has found it utterly impossible to give proper attention to this work, owing to a press of private matters. There are some difficulties in this work. It seems almost impossible to secure coöperation. These difficulties, however, might be overcome by the labors of someone better able to give attention to the matter than I am.

Mr. HUSTON. Mr. Stone wished me to report that his work on abstracts is ready for the typewriter.

The president then called for any discussion upon the report of the abstract committee.

Mr. WILEY. Before the adjournment to-day, I would say that quite a number of the members of the association have asked to have a time set when they could visit our little vegetation house on the Department grounds. I don't know any way to accomplish this but to take time which belongs to the association. I will be pleased to meet any gentlemen who wish to see the experiments at 4 p. m. this afternoon and show what we have there.

After some discussion by the various members, it was finally decided to visit the vegetation house at 12.30 o'clock.

The meeting was then adjourned until 2 o'clock.

FRIDAY—AFTERNOON SESSION.

The meeting was called to order at 2 p. m., with the president in the chair. The recommendations of the reporter on soils was the first business taken up.

Mr. PETER. The first recommendation relates to the separation of gravel from the fine earth. In the preparation of soil it should be sifted first through a sieve of 2 mm. mesh, and a portion of the sifted soil taken and made to pass through a half mm. sieve, rejecting all gravel which will not pass through the sieve.

The PRESIDENT. The recommendation goes to the committee. Do you specify a round or square mesh?

Mr. PETER. Round. The second recommendation is that the Goss method for phosphoric acid be adopted as an alternate method. I am satisfied that the digestion with hydrochloric acid for ten hours does not extract all the phosphoric acid that is really soluble in strong acids. This is shown in soil samples 2 and 4 of the present year. We think the determination of phosphoric acid should be separated from the general analysis.

In the method for nitrogen on page 389, No. 13, instead of "14 grams of soil," read "7 to 14 grams of soil." I think we ought to leave more latitude there in the amount of soil taken for determination.

The method for ash, page 390, under the heading "Analysis of ash," fourth line, for the words, "with 2 or 3 cc of hydrochloric acid," read "with 5 or 10 cc of hydrochloric acid." I think the amount is not enough for the resolution of the residue.

Analysis of ash, page 391, No. 2, insert after the words "50 to 100

cc of solution A," the words, "after the addition of enough ferric chlorid solution to combine with the phosphoric acid present." This is to remedy a very apparent defect in the method as it now stands. If there is an excess of phosphoric acid in the ash above what is necessary to combine with iron and alumina present, we have in the acetic acid filtrate a quantity of calcium phosphate in solution in the acetic acid. This will come down with the manganese. A part of it will go down with the iron and aluminum phosphates; the magnesia will go down impure, and an error will be caused in the lime. It is necessary to remove the phosphoric acid by the addition of ferric chlorid.

The PRESIDENT. The next thing in order is that the recommendations of the reporter on phosphoric acid be taken up and referred to the committee.

Mr. Kilgore mentioned the fact here that some one had found titanium in soils, and the method for phosphoric acid would not work at all in such cases.

Mr. Goss said he supposed it was because of the insolubility of titanium phosphate.

Mr. KILGORE. I don't know. The phosphoric acid goes into solution in the hydrochloric acid, and the titanium also, at least a portion of it, but when it is filtered off and heated to dryness, the titanium combines with the phosphoric acid and forms an insoluble titanium phosphate that is not redissolved by the hydrochloric acid.

The president then asked if the recommendations of the reporter on phosphoric acid were ready.

Mr. KILGORE. I have merely the one I gave before with reference to washing practically free of chlorids and burning to whiteness or gray white. I recommend that the volumetric method be made an alternate method.

Mr. WILEY. I would like to suggest to the committee that they recommend the further trial of direct precipitation of the phosphoric acid with alkaline magnesium citrate. It is used almost exclusively by the German chemists in their official work. It is perhaps not applicable to iron and aluminum phosphates, but I think it ought to be further tried by the association; not that it will displace the official method by the molybdate process, but for commercial and routine work.

Mr. H. B. McDONNELL. Is that method much slower than the molybdate method?

Mr. WILEY. I think as a rule perhaps it may require to stand a little longer, but very few analyses have to be done the same day, and it is no trouble to let it stand over night. It saves work, and is also a valuable reagent. One precipitation is all that is necessary.

Mr. PAYNE. I think the German method quicker where you have a number to make.

Mr. WILEY. Inasmuch as the method is used by so large a body in Europe and has proved so accurate and reliable, I think the committee ought to take some favorable notice of it.

The PRESIDENT. Any other suggestions to the committee?

Mr. FREAR. I would like to say that although I am pleased with the results by the volumetric method, I should feel some hesitation in using it as an alternate method, but should like to see it adopted as a provisional check method.

The PRESIDENT. We will have time to discuss that when reported back from the committee.

The PRESIDENT. Are there any further suggestions? If not, we will pass to the report of the committee on fermented and distilled liquors.

REPORT ON FERMENTED AND DISTILLED LIQUORS.

By GEO. E. COLBY.

FERMENTED LIQUORS.

The following abstract from letter of March 6, 1895, sent to all the experiment stations, explains the work outlined for this study for the year 1895:

It seems advisable to pay particular attention to the determination of glycerol, as difficulty was met with in that part of the work of last year (1894). So it is proposed to determine the glycerol in a red, a white, and a sweet wine, together with as much as can be done upon the following points, viz: Determination of extract (direct and indirect); specific gravity; alcohol (by weight and volume); polarization; acidity (total and volatile); sugar and ash in the samples above named. Then, too, in accordance with the directions of the association, some study on distilled liquors should be started. For that purpose one whisky will be chosen and the determinations of alcohol, specific gravity, extract, and fusel oil in it requested.

The wines selected for the work of this season were white wine, Vernal, from Tulare; red wine, Zinfandel, from Mission San Jose; and sweet wine, sherry, from Mission San Jose—all of the vintage of 1893, and belonging to the class of ordinary wines.

Fourteen orders for samples were filled and dispatched March 26, 1895, with a letter requesting that attention be given to strict observance of association methods of analysis of wine in all the work. Ten reports upon wines were received (W. C. Blasdale, of the University of California, chemical department, and Marvin Curtis, wine chemist, San Francisco, Cal., being the only participants not connected with the Agricultural Department). The results tabulated below were obtained from them:

ANALYSES OF OFFICIAL WINES, 1895.

White wine, Vernal.

Analyst.	Specific gravity.	Alcohol.		Acid.		Extract.		Ash.	Glycerol.	Polarization.		
		By weight.	By volume.	Total, as tartaric.	Volatile, as acetic.	Direct.	Indirect.			Degrees W.	Degrees W. after inversion.	Sugar.
		P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.			P. ct.
G. L. Teller, Arkansas	0.99752	6.56	8.25	2.07	0.990
W. C. Blasdale, California.....	.9972	6.58	8.14	0.622	1.92	0.285	.889
Geo. E. Colby, California.....	.9977	6.72	8.45	.555	0.084	2.18	2.51	.288	.985	— 0.22	— 0.22	0.165
F. T. Bioletti, California.....	.9978	6.58	8.30	.550	.070	2.13	2.51	.296	1.007167
Marvin Curtis, California.....	.99743	6.57	8.29	.487	.080	2.21	2.28	.291	1.000	— .20	— .20

ANALYSES OF OFFICIAL WINES, 1895—Continued.

White wine, Verdal—Continued.

Analyst.	Specific gravity.	Alcohol.		Acid.		Extract.		Ash.	Glycerol.	Polarization.		Sugar.
		By weight.	By volume.	Total as tartaric.	Volatile, as acetic.	Direct.	Indirect.			Degrees W.	Degrees W. after inversion.	
H. J. Patterson, Maryland9973	<i>P. ct.</i> 4.77	<i>P. ct.</i> 5.96	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i> 2.09	<i>P. ct.</i>	<i>P. ct.</i> .300	<i>P. ct.</i> .710	<i>P. ct.</i>
Charles L. Parsons, New Hampshire	6.70	8.34	.560980
R. S. Hiltner, Nebraska99717	6.51	8.18	.569	.078	2.03	1.99	.297	.8599066
W. D. Bigelow, U. S. Department of Agriculture99743	6.61	8.31	.560	.060	2.18	2.12	.260	.603
Elton Fulmer, Washington9976777
Slewinski ¹	1.0082	5.50	6.87	.65	.10	2.02	2.05	.30	.300	.00050

Red wine, Zinfandel.

Analyst.	Specific gravity.	Alcohol.		Acid.		Extract.		Ash.	Glycerol.	Polarization.		Sugar.
		By weight.	By volume.	Total, as tartaric.	Volatile, as acetic.	Direct.	Indirect.			Degrees W.	Degrees W. after inversion.	
G. L. Teller, Arkansas99506	<i>P. ct.</i> 10.54	<i>P. ct.</i> 13.16	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i> 3.00	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i> 1.138	<i>P. ct.</i>
W. C. Blasdale, California9949	10.66	13.29	0.975	2.91	0.221	.696
Geo. E. Colby, California9952	10.44	13.10	.795	.097	3.24	3.10	.208	.926	— .073 —	.073	.282
F. T. Bioletti, California9950	10.49	13.15	.787	.124	3.17	2.87	.210	.818	— .044 —	.044	.264
Marvin Curtis, California9953	10.60	13.29	.710	.080	3.26	3.18	.192	.900
H. J. Patterson, Maryland9955	11.31	14.00	3.14220	1.020
Charles L. Parsons, New Hampshire	10.90	13.50	.850	1.100
R. S. Hiltner, Nebraska99519	10.49	13.16	.868	.152	3.099	2.61	.218	.927	.000187
W. D. Bigelow, U. S. Department of Agriculture99532	10.63	13.33	.730	.054	3.099	3.17	.230	.528	— .070
Elton Fulmer, Washington9955603
Slewinski ¹	1.0112	9.58	11.87	1.17	.08	3.04	2.98430	.600

¹ Reported by George Thoms, Riga, Russia.

ANALYSES OF OFFICIAL WINES, 1895—Continued.

Sweet wine, Sherry.

Analyst.	Specific gravity.	Alcohol.		Acid.		Extract.		Ash.	Glycerol.	Polarization.		
		By weight.	By volume.	Total, as tartaric.	Volatile, as acetic.	Direct.	Indirect.			Degrees W.	Degrees W., after inversion.	Sugar.
G. L. Teller, Arkansas.....	.99128	<i>P. ct.</i> 17.12	<i>P. ct.</i> 21.40	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i> 3.93	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i> .734	<i>P. ct.</i>
W. C. Blasdale, California.....	.9902	17.32	21.27	.600186	.689
Geo. E. Colby, California.....	.9916	17.00	21.25	.540	0.098	4.20	4.15	.204	.700	—2.80	—2.80	2.130
F. T. Bioletti, California.....	.9917	16.85	21.06	.532	.098	4.32	4.40	.191	.770	—2.50	—2.50	1.990
Marvin Curtis, California.....	.99094	17.12	21.37	.490	.045	4.14	4.19	.190	.670	2.130
H.J. Patterson, Maryland.....	.9895	16.51	20.29	4.10210	.790
R. S. Hiltner, Nebraska.....	.99082	17.129	21.386	.631	.054	4.19	13.90	.199	—1.24	—1.24	1.813
W. D. Bigelow, U. S. Department of Agriculture.....	.9907	17.21	21.47	.770	.042	4.024	4.08	.230	.415	—1.26	—1.30
Oma Carr, U. S. Department of Agriculture	34.020
Elton Fulmer, Washington.....	.9905534
Leiste ²9882	15.67	19.28	.654	.038	3.69	3.50	.166	.140	— .90	1.77

¹Schulze.²Reported by George Thoms. Riga, Russia.³Dried with pumice stone in vacuum bath, see below, Extract.

Glycerol.—The tables above show 28 results for this year's work, for three wines, and each sample has received more attention in this respect than did the official wine of last year. The results indicate that this determination will bear considerably more study.

Note by G. L. Teller.—The crude glycerol obtained from the sweet and the white wines was redissolved in absolute alcohol and reprecipitated several times with ether, with these results:

	Sweet wine.	Red wine.
	<i>Gram.</i>	<i>Gram.</i>
First precipitation.....	0.668 and 0.800	0.973 and 1.008
Second precipitation.....	.650 and .722	.951 and .917
Third precipitation.....	.616 and .700	.851 and .849
Fourth precipitation.....	.614 and .679	.804 and .801
Fifth precipitation.....	.607 and .595

Extract.—The results for all the wines, as far as they go, are very satisfactory.

Note by Oma Carr.—Concerning my determinations of extract in the official wines, conducted by the pumice-stone method in vacuo, I beg to report as follows:

Sherry.

	Per cent extract.	
Dried three hours.....	4.14	and 4.15
Dried four hours.....	4.017	and 4.030

No alternation of weight up to nine hours of drying. Dried approximately 3 grams material in flat aluminum dishes on layer of fine pumice stone (not powdered) in vacuum bath. Temperature, 70°; vacuum, 24 inches; temperature in excess of boiling point, 10°.

The pumice-stone method, briefly stated, consists in the employment of small fragments of acid-washed stone, upon which, after ignition, cooling, and weighing, the material is distributed from a weighing bottle. The drying is conducted in vacuo, the temperature never being raised to above 10° in excess of the boiling point corresponding to the vacuum. Operating with a vacuum of 24 inches, the temperature should be 70°; for a vacuum of 25 inches, 67°; for 26 inches, 62°; for 27 inches, 56°, etc. In weighing, the dishes are covered with a ground-glass plate.

Comparing these figures just above with the average direct extract for the sherry, 4.11 per cent, we might consider Mr. Carr's work for this wine an excellent verification of the results yielded by the regular method.

Specific gravity.—The results for the red and the white wines are respectively very close; those for the sherry show some differences, but are in accordance with what should be expected.

Alcohol.—The figures returned for this important constituent show differences which are admissible (with the exception of those from one station) and should be considered quite satisfactory.

Note by W. D. Bigelow.—I give also the amount of alcohol with and without the use of the mercury valve:

Alcohol by volume.	Verdal.	Zinfandel.	Sherry.
With mercury valve.....	8.31	13.33	21.47
Without mercury valve.....	8.33	13.28	21.44

You will observe that these results are so close together that they would be entirely satisfactory as duplicates, and as each of the results given in this comparison is a mean of from three to six separate determinations, I am more strongly inclined than ever to regard the valve as superfluous.

Acidity.—Fairly concordant results are reported for the total acid; the volatile acid has received but little attention this year. W. D. Bigelow used cochineal indicator, but considers "that it is not satisfactory, because the end reaction is not sharp."

Note by Geo. E. Colby.—In order to shorten the work and to use less apparatus than called for by the regular method, I have been in the habit of determining the volatile acid either in 5 cc or 10 cc of wine, to which has been added 5 cc or 10 cc saturated solution of pure sodium sulphate (to raise the boiling point), and heating in a beaker with watch-glass cover till distillate on cover shows no acidity, and finally titrating. The difference (cc N-10 alkali) between the total and this titration is calculated as acetic acid.

The official wines treated in the above manner give results tabulated below, which resemble closely those obtained by the regular method.

Volatile acid (as acetic).	Verdal, white wine.	Zinfandel, red wine.	Sherry, sweet wine.
Determined by association method.....	0.084	0.097	0.098
Determined with sodium sulfate, as above described.....	.084	.102	.108

Ash.—All the results are very close.

Polarization and sugar.—Not sufficient data have been received to make it possible to discuss the results.

DISTILLED LIQUORS.

At my request my associate, Mr. W. D. Bigelow, planned and directed the work with distilled liquors. A sample of artificial rum was prepared by the addition of a known amount of fusel oil, flavoring material, and caramel, to fusel free alcohol, which had been previously distilled over caustic potash, and diluted to a little below proof. Analysis of the fusel oil used gave the following results:

	Per cent.
Amyl alcohols.....	43.67
Butyl alcohols	10.96
Propyl alcohols	18.25

Of this fusel oil, 25.3 cc were added to 12 liters of the diluted alcohol, thus making 0.210 per cent of the fusel oil, or 0.153 per cent of the higher alcohols, which I shall hereafter designate as fusel oil. Samples of this rum were sent to eighteen analysts, from ten of whom reports were received.

A letter was sent with each sample requesting that especial attention be given to the determination of fusel oil, and giving detailed directions for this determination according to Dupré's method. Six analysts reported results by this method, two by Marquardt's method and five by Herzfeld's modification of Roese's method. In addition to these, two reported their inability to obtain concordant results by Dupré's method and one by Marquardt's method.

The results obtained are given in the following table:

Analyst.	Specific gravity.	Alcohol by weight.	Ex-tract.	Fusel oil.			
				Dupré.	Mar-quardt.	Roese-Herzfeld.	Amount added.
		<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per cent.</i>	<i>Per cent.</i>
G. L. Teller, Arkansas	0.94646	36.54	0.120
W. C. Blasdale, California.....	.94633	36.25	0.463
F. T. Bioletti, California.....	.94610	36.14	.130	¹ .269
Do	² .238
Wm. Bromwell, Museum of Hygiene, Washington, D. C.....	0.108
Geo. E. Colby, California94600	37.05	.130	.640	0.601
Fassbender, Landw.-chem. Ver- suchsst., Kempen am Rhein.....	.94640	34.17	.125660
F. H. Wernskiold, Kemiske Kontrol- stat., Christiania, Norway.....	36.70135
G. Thoms, Chem. Versuchsst., Riga.....0265
Robt. S. Hiltner, Nebraska94605	36.64	.133	¹ 1.018
Do	² 1.044
W. D. Bigelow, U. S. Department of Agriculture.....	.94562	36.87	.128	¹ .180	.157	.140
Do	¹ .136	.139	.127
Do	¹ .205	.177	.135
Do	² .230
Do	² .285
Oma Carr, U. S. Department of Agri- culture.....	³ .153
H. B. McDonnell, Maryland341
Do331
Theory.....	.94584	36.76	.129	.187	.156	.179	0.153

¹ With previous distillation.

² Without previous distillation.

³ Obtained by pumice-stone method in vacuo.

The difference between the figures given as theory and the amount added will be understood when the methods of calculation employed by the various authors are remembered.

All the determinations except that of fusel oil are fairly satisfactory, though it is worthy of note that the extract as determined by Mr. Carr by the pumice-stone method in vacuo is decidedly higher than that reported by the official method. The results reported on the determination of fusel oil emphasize the necessity of further work upon this subject.

REMARKS AND EXTRACTS FROM REPORTS.

Charles L. Parsons.—The analysis (Dupré's method) is very tedious, and I do not think will ever be much used in its present form. The time required to make the distillations is very trying, and the multiplied chances of loss too great for accurate work, in my opinion, even if valeric acid means fusel oil after the work is done.

G. L. Teller.—A considerable number of trials for fusel oil were made, and though the work was carried on with great care the results were so discordant that none are given. In my hands the method (Dupré's) has proven very tedious and unsatisfactory.

Geo. E. Colby.—Where the results are obtained from work done in duplicate it seems to me that this method (Dupré's) should be good, but it is very certain that a great deal of experience is required for its use, especially when investigating commercial articles.

Wm. Bromwell.—My results by the Marquardt method, which was tried several times, were so discordant as to make them of no value except to show that the method is of little use if followed exactly as given. I am inclined to think that some valuable modifications might be made in it which would make it more useful. I am not, however, prepared to suggest them at present. The fact that some of the ethyl alcohol is extracted by chloroform in proceeding as described in the method as given by Allen in the second edition of his *Commercial Organic Analysis* was clearly shown by a strong odor of acetic acid in the course of the operations following the oxidation of the chloroform extract. This was observed in running a blank with fusel-free alcohol of specific gravity 0.980.

By the Roese-Sell-Windisch method I obtained results which are more concordant. There are two points in this method, however, to which I should like to call attention: First, the large error introduced by slight changes in the temperature of the bath; and to render such changes less liable to occur, I would suggest that the method be so modified as to be used at a temperature higher than 15°, say at 25°, which is a temperature much more easily maintained in our laboratories. Second, it is quite difficult to introduce the chloroform into the apparatus satisfactorily by using a drawn-out funnel or pipette, and I would suggest as a remedy for this trouble that the apparatus be so made that the chloroform could be sucked up into the bulb exactly to the 20 cc mark and kept there by turning a stopcock. This could easily be done by sealing a small tube fitted with a stopcock to the lower end of the bulb.

I would recommend: First, that in the alcohol determination the use of the mercury valve be discontinued; second, that in the glycerol determination there be added to the method, after the words "water oven," the following: "and weighed, the ash determined in it, and its weight deducted from that of the weighed residue;" third, that the directions for the determination of alcohol be made to read as follows:

II. DETERMINATION OF ALCOHOL—

(a) In fermented liquors.

(1) *By weight.*—One hundred cc of the liquor are measured into a flask of from 250 to 300 cc capacity, 50 cc of water added, the flask attached to a vertical condenser by means of a bent tube, and 100 cc distilled. The specific gravity of the

distillate is determined as directed under "Determination of specific gravity of liquors." The distillate is also weighed or its weight calculated from the specific gravity. The corresponding percentage of alcohol by weight is obtained from the appended table, and this figure multiplied by the weight of the distillate and the result divided by the weight of the sample taken gives the per cent of alcohol by weight.

(2) *By volume*.—The percentage of alcohol by volume of the liquor is the same as that of the distillate, and is obtained from the appended table.

(b) In distilled liquors.

(1) *By weight*.—About 30 grams of the liquor are weighed, diluted to 150 cc, 100 cc distilled, and the per cent of alcohol by weight determined as under fermented liquors.

(2) *By volume*.—The percentage of alcohol by volume in the distillate is obtained from the appended table, this figure divided by the volume of the liquor taken for the determination (calculated from the specific gravity), and the result multiplied by 100.

The PRESIDENT. Are there any remarks or papers?

Mr. HUSTON. Was any examination made of the pharmacopœias and dispensatories to see how their methods compared with our own?

Mr. BIGELOW. Not for distilled liquors. The pharmacopœia does not take into consideration the fusel oil, but does consider the specific gravity, extract, and percentage of alcohol.

Mr. PAYNE. The determination of fusel oil and aldehyds is a valuable line of work. I had something to do with revising a pharmacopœia, and on these particular subjects there seems to be very little known.

Mr. BIGELOW. I neglected to mention that at the bottom of page 373, Bul. 43, under "Polarization," there is something wrong with the factors given there. They are not correct. I suggest that the correct factors be substituted, and that they be expressed in terms of angular rotation.

It was voted that Mr. Bigelow, as a member of the editing committee, be empowered to make the substitution.

The PRESIDENT. The recommendations of the reporter were included in his report, and, unless requested, the recommendations will not be read, but will be considered as before the committee. We have only about ten minutes now before the special order of business for 3 o'clock. I suggest that as there is hardly time to take up the nitrogen report, we might hear from the committee on editing methods.

REPORT OF THE EDITING COMMITTEE.

By L. L. VAN SLYKE and W. D. BIGELOW.

ORDER OF GIVING METHODS.

- I. Methods for the analysis of fertilizers.
- II. Methods for the analysis of foods.
- III. Methods for the analysis of dairy products.
- IV. Methods for the analysis of soils.
- V. Methods for the analysis of ashes.
- VI. Methods for the analysis of sugars.
- VII. Methods for the analysis of fermented and distilled liquors.
- VIII. Methods for the analysis of tanning materials.

I. METHODS FOR THE ANALYSIS OF FERTILIZERS.

1. Preparation of samples.
2. Determination of moisture.
3. Determination of phosphoric acid.
 - (a) Preparation of reagents.
 - (b) Total phosphoric acid.
 - (1) Methods of making solution, (A), (B), (C), (D), (E), (F).
 - (2) Determination.
 - (c) Water-soluble phosphoric acid.
 - (d) Citrate-insoluble phosphoric acid.
 - (1) In acidulated goods.
 - (2) In nonacidulated goods.
 - (e) Citrate-soluble phosphoric acid.
4. Determination of nitrogen.
 - (a) Kjeldahl method (nitrates absent).
 - (1) Reagents.
 - (2) Apparatus.
 - (3) Determination.
 - (b) Gunning method (nitrates absent).
 - (1) Determination.
 - (c) Kjeldahl method modified to include the nitrogen of nitrates.
 - (1) Reagents.
 - (2) Determination.
 - (d) Gunning method modified to include the nitrogen of nitrates.
 - (1) Determination.
5. Determination of potash.
 - (a) Reagents.
 - (1) Preparation of NH_4Cl solution.
 - (2) Preparation Pt Cl_4 solution.
 - (b) Solution.
 - (1) In case of potash salts and mixed fertilizers.
 - (2) In case of organic compounds.
 - (c) Method of Lindo-Gladding.
 - (1) In mixed fertilizers.
 - (2) In muriate of potash.
 - (3) In sulphate of potash, kainit, etc.
 - (d) Optional method.
 - (e) Factors.

II. METHODS FOR THE ANALYSIS OF FOODS.

1. Preparation of sample.
2. Determination of moisture.
3. Determination of ash.
4. Determination of ether extract.
 - (a) Reagents, preparation of anhydrous ether.
 - (b) Direct method.
 - (c) Indirect method.
5. Determination of crude protein.
6. Determination of albuminoid nitrogen by Stutzer's method.
 - (a) Reagents, preparation of cupric hydrate.
 - (b) Determination.
7. Determination of crude fiber.

III. METHODS FOR THE ANALYSIS OF DAIRY PRODUCTS.

1. Analysis of butter.
 - (a) Microscopic examination.
 - (b) Sampling.
 - (c) Determination of water.

III. METHODS FOR THE ANALYSIS OF DAIRY PRODUCTS—Continued.

1. Analysis of butter—Continued.

- (d) Determination of fat.
 - (1) Direct method.
 - (2) Indirect method.
- (e) Determination of casein and ash.
- (f) Determination of salt.
- (g) Determination of specific gravity.
- (h) Determination of melting point.
 - (1) Reagents.
 - (2) Apparatus.
 - (3) Determination.
- (i) Determination of volatile acids.
 - (1) Reagents.
 - (2) Apparatus.
 - (3) Determination.
- (j) Optional method of determining volatile acids.
- (k) Determination of iodine absorption number.
 - (1) Reagents.
 - (2) Determination.
- (l) Optional methods of butter analysis.

2. Analysis of milk.

- (a) Determination of water.
- (b) Determination of total nitrogen compounds.
- (c) Determination of total solids.
- (d) Determination of fat.
 - (1) By Babcock asbestos method.
 - (2) By paper-coil method.
- (e) Determination of sugar.
 - (1) Optical method.
 - (A) Reagents.
 - (B) Apparatus.
 - (C) Determination.
 - (2) Optional methods. It is recommended that special tables adapted to milk sugar be inserted.
- (f) Determination of ash.

3. Analysis of cheese; provisional methods.

- (a) Sampling.
- (b) Determination of water.
- (c) Determination of ash.
- (d) Determination of fat.
- (e) Determination of nitrogen compounds.
- (f) Determination of other constituents.

IV. METHODS FOR THE ANALYSIS OF SOILS.

- 1. Sampling (should be given).
- 2. Preparation of sample.
- 3. Determination of moisture.
- 4. Determination of volatile matter.
- 5. Determination of acid-soluble materials.
 - (a) Acid digestion of soil.
 - (b) Determination of ferric oxide, alumina, and phosphoric acid, collectively.
 - (c) Determination of manganese.
 - (d) Determination of lime.
 - (e) Determination of magnesia.

IV. METHODS FOR THE ANALYSIS OF SOILS—Continued.

5. Determination of acid-soluble materials—Continued.
 - (f) Determination of ferric oxid.
 - (g) Determination of phosphoric acid.
 - (h) Determination of sulfuric acid.
 - (i) Determination of potash and soda.
6. Determination of acid-insoluble materials.
7. Determination of total alkalies.
8. Identification of caesium, lithium, and rubidium.
9. Determination of total nitrogen.
10. Determination of carbon dioxide.
11. Determination of humus.
12. Determination of hygroscopic coefficient.
13. Mechanical analysis.
14. Water capacity.
15. Capillary power and water soluble materials.
16. Mechanical analysis.

} Should be amplified.

V. METHODS FOR THE ANALYSIS OF ASHES.

1. Preparation of ash.
2. Analysis of ash.
 - (a) Carbon, sand, and silica.
 - (b) Manganese, lime, and magnesia.
 - (c) Phosphoric acid.
 - (d) Sulfuric acid and alkalies.
 - (e) Carbon dioxide.
 - (f) Chlorin.

VI. METHODS FOR THE ANALYSIS OF SUGARS.

1. Determination of water.
 - (a) In sugar or masse cuite.
 - (b) In honey or molasses.
2. Determination of ash.
3. Determination of nitrogen.
4. Determination of reducing sugars.
 - (a) Reagents.
 - (b) Approximate volumetric method for rapid work.
 - (c) Soxhlet's exact volumetric method.
 - (d) Gravimetric method for materials containing 1 per cent or less of invert sugar.
 - (e) Gravimetric method for materials containing more than 1 per cent of invert sugar.
 - (f) Allihn's gravimetric method for the determination of dextrose.
5. Determination of sucrose.
 - (a) Preparation of reagents.
 - (b) Optical method.
 - (1) In sugars, masse cuites, etc.
 - (2) In juices, etc.
 - (c) Determination.
 - (1) Optical methods by inversion.
 - (A) Method of Clerget.
 - (B) The official German method.
 - (C) Method of Lindet.
 - (2) Gravimetric method.

VII. METHODS FOR THE ANALYSIS OF FERMENTED LIQUORS.

1. Determination of specific gravity.

VII. METHODS FOR THE ANALYSIS OF FERMENTED LIQUORS—Continued.

2. Determination of alcohol.
 - (a) By weight.
 - (b) By volume.
3. Determination of extract.
 - (a) In dry wines, beers, ales, etc.
 - (b) In sweet wines.
4. Determination of total acidity.
5. Determination of volatile acids.
6. Determination of glycerol.
 - (a) In dry wines.
 - (b) In sweet wines.
7. Determination of reducing sugars.
 - (a) Preliminary test.
 - (b) Final determination.
 - (c) Allihn's method.
8. Polarization.
 - (a) In white wines.
 - (b) In red wines.
 - (c) In sweet wines.
 - (1) Before inversion.
 - (2) After inversion.
 - (3) After fermentation.
 - (d) Application of analytical method.
9. Determination of tannin and coloring matter.
10. Determination of potassium bitartrate.
11. Determination of tartaric, malic, and succinic acids.
 - (a) Schmidt and Hiepe's method.
 - (b) Modified Berthelot Fleury method.
 - (c) Determination of tartaric acid in filtrate from 10.
12. Determination of coloring matter.
 - (a) Fuchsin.
 - (b) Sodium rosanilin sulfonate.
13. Inorganic matter.
14. Citric acid.
15. Sulfuric acid.
16. Chlorin.
17. Calcium and magnesium.
18. Phosphoric acid.
19. Potash.
20. Gum and dextrin.
21. Sulfurous acid.
22. Salicylic acid.

VIII. METHODS OF ANALYSIS OF TANNING MATERIALS.

1. Testing the hide powder.
2. Moisture in sample.
3. Provisional method.

The report was adopted as a whole.

The president now called for the report of the committee on nominations.

Mr. Winton gave the nominations of the committee as follows: For president, Mr. B. B. Ross; for vice-president, Mr. William Frear; for secretary, Mr. H. W. Wiley; executive committee, Mr. H. J. Wheeler, Mr. F. W. Traphagen.

The recommendations of the committee on nominations were voted upon and adopted.

The president then suggested that any business outside of reports be brought forward at this time.

Mr. WILEY. I move that the thanks of the association be extended to the authorities of the National Museum for the use of this lecture hall.

Motion seconded and carried.

Mr. BARTLETT. There seems to be a misunderstanding as to whether a reporter is to serve one or two years after this year. I would like to have this explained.

The PRESIDENT. I think I had better let my successor explain that. We adopted this duplicate reporter system with the understanding that the reporter who was associate one year would be the reporter proper on the subject the following year.

The president then called for the report on nitrogen.

REPORT ON NITROGEN.

By J. M. BARTLETT, *Reporter*.

In accordance with a vote of the association at its last meeting that the reporters for 1894 should serve for 1895, I again assumed the duties as reporter on nitrogen for this year. As was the case last year, the members were very chary of instructions in this line of work, and a few suggestions on testing methods for nitric nitrogen and the Fassbender method for total nitrogen in presence of nitrates made by the reporter of last year were all that I received.

Notwithstanding that I fully appreciate the fact that one of the most important problems before us is, How to determine the availability of nitrogen in mixed fertilizers, still there seems to be no method even yet in shape for the chemists to test in a practical way. It is to be hoped, however, that before the next meeting of the Association of Official Agricultural Chemists a fairly reliable and practical method will be devised.

It seems quite reasonable that as all organic nitrogen in the soil must undergo the oxidation process to become available to plants, it would be possible to imitate that process to a fairly accurate degree by oxidizing agents in the laboratory.

A circular letter was sent out early in December asking cooperation of all official chemists, and suggestions for the work on nitrogen. The suggestions failed to materialize, but about twenty chemists applied for samples; consequently a sample to answer the requirements of the suggestions heretofore mentioned was made up as follows:

Very finely pulverized dried blood, cotton-seed meal, bone dust, South Carolina rock and enough c. p. sodium nitrate to make 2 percent nitric nitrogen were very intimately mixed, put in bottles, and sealed. The mixing was done so thoroughly that it seems impossible that the samples could vary unless there was mechanical separation after the material was put in the bottles. To all applicants samples were sent, and also the following letter of instructions:

I send you by express two samples of material for the association work on nitrogen. Sample No. 1 is a portion of the material used last year and contains 4.71 per cent of nitrogen (1.91 in form of nitrate). You are requested to test your standard solutions, reagents, etc., by making a nitrogen determination in this sample. By so doing we hope to obtain very closely agreeing results on sample No. 2. In sample No. 2 determine total nitrogen by either the Kjeldahl or Gunning methods, modified for nitrogen of nitrates, as given on page 347, Bulletin No. 43, United States Department of Agriculture, Division of Chemistry. Also, if you have the opportunity, by the method employed by Dr. Fassbender, given on page 138 of the same Bulletin.

Determine nitric nitrogen—

First, by the following method: Weigh off 1 gram of sample in a flat-bottomed, 500 cc flask. Add 2 to 5 grams of reduced iron, 25 cc of water, and 5 to 10 cc of sulfuric acid (sp. gr. 1.35). Shake well, close the neck of the flask with a rubber stopper in which has been inserted a dropping-bulb. (See Ulsch's method.) Boil for five minutes rinse the contents of the bulb into the flask, add about 150 cc of water, a little paraffin, and 3 grams of heavy magnesium oxid. Distill for forty minutes, and proceed as usual. The nitrogen obtained represents the nitrates and the ammonia contained in the sample, from which result the amount of nitric nitrogen can be obtained by deducting the percentage of ammonia found. By allowing the boiling to begin very slowly all danger of foaming is avoided.

Second, by the zinc-iron method, so called, given on page 142 of Bulletin No. 43, using 10 grams of the material instead of 5, as in the case of pure nitrates, and filtering through a dry filter before taking a portion for analysis.

You are especially requested to make the determinations of nitric nitrogen, as the association wishes to adopt one of the methods if either is found to be satisfactory.

Reports were received from eleven analysts, and their results are given in tabular form below.

	Sample No. 1.				Sample No. 2.			
	Total nitro- gen.		Nitric ni- trogen.		Total nitro- gen.		Nitric ni- trogen.	
	Official method.	Fassbender method.	Ulsch-Street method.	Zn-Fe method.	Official method.	Fassbender method.	Ulsch-Street method.	Zn-Fe method.
Agricultural Department, Washington, D.C., T. C. Trescot, analyst	¹ 4.88	1.91	¹ 4.59	1.85
	² 4.76		1.96	² 4.45		1.87
	³ 4.75	⁴ 1.91	³ 4.43	⁴ 1.88
	⁵ 4.72	⁴ 1.91	⁵ 4.44	⁴ 1.85
	⁶ 1.71	⁶ 1.80
New Hampshire Station, E. P. Stone, analyst	4.85	4.60	⁷ 4.25	⁷ 1.48	2.02
	4.81	4.71	⁷ 1.52	2.05
	⁷ 1.42	1.98
Montana Experiment Station: F. W. Traphagen, analyst	4.73	1.87	1.96	4.60	2.06	1.96
	4.78	1.94	2.02	4.61	2.10	1.95
	4.75	2.00	2.03
	2.07	1.96
W. M. Cobleigh, analyst	4.52	1.98
Illinois Experiment Station, C. G. Hopkins, analyst	4.70	1.86	4.62	1.98
	4.69	1.88	4.63	1.97
	4.69	1.88	4.66	1.96
	4.74	1.90	4.49	1.94
	1.90	4.51	1.94
	4.47	1.94
Maryland Agricultural College, H. C. Sherman, analyst	4.67	4.71	4.51	4.46	1.99	1.93
	4.68	4.56	4.47	2.03	2.02
	4.71	4.63	4.53	2.13
Virginia Agricultural Experiment Station: A. T. Eskridge, analyst	4.54	1.71
	4.33
W. B. Ellett, analyst	4.51	1.72
	4.34

¹ Absolute method.² Kjeldahl method.³ Kjeldahl method with Hypo.⁴ Ulsch-Street modified by Bartlett.⁵ Gunning method.⁶ Only 3 grams MgO used.⁷ Omitted from averages.

	Sample No. 1.				Sample No. 2.			
	Total nitro- gen.		Nitric ni- trogen.		Total nitro- gen.		Nitric ni- trogen.	
	Official method.	Fassbender method.	Ulsch-Street method.	Zn-Fe method.	Official method.	Fassbender method.	Ulsch-Street method.	Zn-Fe method.
New Jersey Experiment Station, J. P. Street, analyst	4.75	4.73	1.90	4.53	4.50	2.01
	4.68	4.73	1.86	4.55	4.53	1.99
	4.77	1.90	4.61	4.56	2.01
	4.72	4.55	2.01
	4.71	1.99
North Carolina Experiment Station, F. B. Carpenter, analyst.....	4.65	1.91	1.92	4.47	2.00	2.00
	4.68	1.86	1.90	4.46	2.03	2.02
	4.68	4.50	2.02	2.02
	4.68	4.48	1.95
	4.69	4.49
	4.52
Maine Experiment Station:								
L. H. Merrill, analyst.....	4.55	4.47
J. M. Bartlett, analyst.....	4.74	4.66	1.87	1.95	4.55	4.55	2.04	2.02
	1.89	1.90	2.02	2.00
	1.95	1.98
	1.97	2.00
	1.93	2.01
Michigan Experiment Station	4.69	4.51	2.03	2.03
	4.73	4.52	2.05
	4.71	4.49
	4.73	4.53
	4.63	4.49
	4.66	4.52
Average	4.73	4.71	1.90	1.91	4.52	4.51	1.98	1.98

COMMENTS OF ANALYSTS.

H. W. Wiley.—In determining nitric nitrogen by the modified Ulsch method, we obtained better results with a larger quantity of MgO than 3 grams.

F. B. Carpenter.—My first determinations by the modified Ulsch method were lower than those given above, due probably to incomplete distillation. The results given were obtained by distilling nearly to dryness, using 5 to 7 grams MgO. It also seems necessary to agitate the flask occasionally while the digestion with H_2SO_4 and iron is going on, that the material may be washed down from the sides of the flask. By using proper precautions the method gives good results, but I believe there is more liability of error than with the zinc-iron method, with which I experienced no difficulty.

R. J. Davidson.—The Ulsch method with us proved very unsatisfactory, but we had no heavy MgO, and possibly that may have been the cause of our poor results.

E. P. Stone.—In determining the total nitrogen by the Fassbender method, I could get no good results.

C. G. Hopkins.—My results obtained from the samples when the bottles were full were higher than those obtained later when the bottles were nearly empty, due I think to mechanical separation. In working the modified Ulsch method, I found it

better to take 10 grams, dissolve, make up to 250 cc, and take 25 cc for a determination, then using NaOH for the distillation instead of MgO; 25 cc of NaOH solution was used, and the whole diluted to 250 cc, then the distillation was quickly made and solution did not become concentrated.

H. C. Sherman.—In the Ulsch method, 5 grams MgO were used; 3 grams gave low results. The Ulsch method for nitric nitrogen was more satisfactory than the zinc-iron. It is much more rapid and gives, if 5 grams of magnesia are used and distillation carried nearly to dryness, more concordant results. In working the zinc-iron method, it was extremely difficult to prevent soda being carried over mechanically.

The Fassbender method for total nitrogen seems to give very good results if the sample is first thoroughly mixed with water and, after adding iron and dilute sulfuric acid, allowed to stand for half an hour before heat is applied or strong acid added; otherwise the results are low. On account of the nature of sample No. 2 it was very difficult to mix thoroughly with water, and this probably accounts for the slightly low results. As both of the official methods commonly used depend upon the fixation of nitric nitrogen by salicylic acid, while this does not, it would probably be useful as a check method.

F. W. Traphagen.—In the magnesia method, digested in 500 cc Kjeldahl flask, using the bulb tube in place of dropping-tube suggested, after the five minutes digestion with reduced iron, washed this tube with H_2O , added water to flask, then added the water and MgO and distilled from same flask through same bulb tube. This tube is the ordinary single bulb. Used no asbestos plug.

In zinc iron method used same bulb tubes without plug.

If results are reliable, would much prefer the magnesia method on account of ease of manipulation and saving of time.

R. C. Kedzie.—In the Kjeldahl method we put the acid in the digestion flask before putting the substance in, and by this method we find mixing much easier. Substance and acid are mixed and allowed to stand about an hour at room temperature before heating. With the Ulsch method for nitric nitrogen we found it necessary to use 6 grams of MgO.

REPORTS OF FOREIGN CHEMISTS.

Two reports only from foreign chemists have been received:

Dr. F. H. Wernskiold, of Christiania, Norway.—Sample No. 2: Total nitrogen, 4.56, by Kjeldahl-Jodlbauer method; nitric nitrogen, 1.48, by Schloesing's method.

Dr. Fassbender, of the Experiment Station at Kempen on the Rhine.—Sample No. 2:

	Per cent.		Per cent.
Total nitrogen.....	{ 4.66	Nitric nitrogen.....	{ 2.22
	{ 4.72		{ 2.22
Mean	4.69	Mean	2.22

The total nitrogen was estimated by the method given by Fassbender in his last year's report. The nitric nitrogen was estimated as follows:

In a shallow tin-foil schaelchen, place 1 gram of the fine-ground material and add 3 cc of a 50 per cent sulfuric acid solution, and stir well with a small glass rod. Dry for four hours at a temperature of from 60° to 80°, and then for one hour at a temperature of from 120° to 130°. The moist mass remaining in the schaelchen is by this process rendered completely free of nitric nitrogen. The schaelchen and its contents are next placed in an oxidation flask of the Kjeldahl pattern, and subjected to moist combustion with sulfuric acid. The percentage of nitrogen obtained subtracted from the original percentage gives the percentage of nitric nitrogen. In the case mentioned, the original nitrogen was 4.69 per cent. After treatment as above, the nitrogen was 2.47 per cent; difference equals 2.22 per cent, representing the total nitric nitrogen.

DISCUSSION OF RESULTS.

The results as a whole are very satisfactory and show great improvement over those obtained a few years ago. Out of thirty-four determinations of total nitrogen on sample No. 2, by the official methods, thirty are within 0.1 per cent of the average. Of the remaining four, one is 0.18 higher, one 0.2 lower, one 0.19 lower, and one 0.12 higher. Three of these results could hardly be called passable for nitrogen work, but aside from these it would be very difficult to find a lot of determinations made by so many different men agreeing so closely. With one exception the analysts who tried the Fassbender method were much pleased with it. If it proves always reliable, as it seems to be, I should much prefer it to any other method now in use in presence of nitrates, as the digestion can be completed in much less time.

Mr. Street and Mr. Merrill have used the method in their regular work beside the official methods--the best test that can be applied to a method--and as will be seen by the results given, it worked very satisfactorily. There were two samples, however, high in nitrogen, that gave Mr. Merrill considerable trouble, and he obtained several results by the Fassbender method that were too low, but by digesting for quite a long time on the steam bath before adding strong acid, good results were finally obtained.

The two methods for determining nitric nitrogen on trial have given quite satisfactory results in the hands of most of the chemists. As will be seen by their remarks, the chemists are about evenly divided as to choice of methods.

Both processes seem to be perfectly reliable when properly worked.

I much prefer the Ulsch myself, as it is more rapid and requires less attention when making the distillation. I found no difficulty in making a distillation in thirty minutes when I used 5 grams of the light MgO ; 3 grams does not seem to be sufficient. I think that possibly it would be well to take 5 or 10 grams of the substance, leach the nitrate out from the organic matter, and take an aliquot part for the determination; then distill with $NaOH$. There would be less liability of incomplete distillation, and the ammonia could be determined in a portion of the same solution. The method for determining nitric nitrogen presented by Dr. Fassbender this year may be worthy of our consideration, as it does not require the determination of ammonia.

RECOMMENDATIONS.

(1) I recommend that the Ulsch-Street method, as given in my circular letter, except that 5 grams of MgO be used instead of 3, be made an official method for determining nitric nitrogen.

(2) That the $Zn-Fe$ method be made an alternate method for determining nitric nitrogen.

(3) That the association print a method--the MgO method--for determining ammonia in presence of organic nitrogen.

I also suggest that, in view of the fact that the Fassbender method for determining nitrogen in presence of nitrates promises so well, those chemists engaged in work on fertilizers test it beside the official methods with a view to adopting as an official method next year.

Table comparing the Fassbender with the official method in regular work.

[By L. H. Merrill.]

Gunning.	Fassbender.	Difference.	Gunning.	Fassbender.	Difference.	Gunning.	Fassbender.	Difference.
<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
2.21	2.27	+ .06	1.96	1.94	— .02	2.82	2.70	— .12
2.86	2.79	— .07	4.08	4.13	+ .05	1.99	1.93	— .06
2.05	2.05	2.30	2.39	+ .09	1.07	1.10	+ .03
2.03	2.05	+ .02	3.50	3.57	+ .07	2.90	2.86	— .04
3.61	3.55	— .06	2.43	2.48	+ .05	2.25	2.28	+ .03
2.26	2.19	— .07	4.77	4.82	+ .05	2.70	2.68	— .02
2.13	2.05	— .08	1.00	1.00	2.07	1.99	— .08
2.30	2.30	2.01	1.96	— .05	2.72	2.70	— .02
2.17	2.10	— .07	1.16	1.10	— .06	2.04	2.04
3.39	3.39	3.24	3.15	— .09	1.29	1.20	— .09
2.07	2.05	— .02	1.00	.94	— .06			

In nine cases Fassbender gave higher results, averaging 0.05; in eighteen cases Fassbender gave lower results, averaging 0.06; in five cases Fassbender gave same results. For the thirty-two cases the average was 0.2 per cent lower for the Fassbender.

Table comparing Fassbender's with the official method in regular work.

[By J. P. Street.]

FASSBENDER'S HEATED.

Official method.	Fassbender method.	Official method.	Fassbender method.	Official method.	Fassbender method.	Official method.	Fassbender method.	Official method.	Fassbender method.
<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
3.58	3.67	2.89	2.87	3.41	3.42	3.60	3.69	1.99	2.05
3.20	3.20	3.61	3.64	3.73	3.75	3.00	2.96	2.88	2.87
3.39	3.48	2.51	2.57	2.59	2.54	3.96	3.99	4.94	4.98
7.90	7.99	2.60	2.62	2.45	2.38	4.90	4.98	4.47	4.58
2.47	2.57	2.41	2.38	1.23	1.26	3.21	3.31	4.59	4.66
3.74	3.81	2.85	2.91	7.11	7.09	2.51	2.49	3.59	3.61
2.89	2.81	2.35	2.34	3.28	3.17	3.06	3.14	1.87	1.84
3.38	3.41	1.03	1.00	1.20	1.18	3.06	2.10	2.66	2.70
3.85	3.90	1.91	1.84	4.85	4.80	3.00	3.06		
3.62	3.71	3.57	3.67	1.96	1.88			13.04	13.07

FASSBENDER'S NOT HEATED.

3.03	2.94	2.48	2.55	2.93	2.91	6.45	6.37	2.52	2.64
2.72	2.77	2.43	2.42	2.46	2.52	3.52	3.51	1.17	1.24
2.24	2.21	2.12	2.10	2.69	2.78	3.12	3.14	2.48	2.44
.97	.98	2.31	2.22	2.56	2.63	3.33	3.23	2.10	1.99
2.51	2.51	3.39	3.44	3.87	3.96	2.91	2.99	1.21	1.29
.73	.71	2.91	2.93	4.43	4.51	2.64	2.74	2.81	2.85
3.41	3.44	3.94	4.02	4.68	4.71	2.22	2.12	7.51	7.59
1.42	1.43	2.71	2.74	2.85	2.87	2.28	2.32	4.15	4.24
1.67	1.68	2.71	2.76	3.16	3.21	2.95	3.04	3.53	3.56
3.74	3.65	1.60	1.58	1.33	1.33	1.96	1.89	2.16	2.14
1.80	1.80	3.39	3.46	2.16	2.22	3.14	3.11		
3.02	2.91	3.09	3.08	2.58	2.57	3.08	3.11	12.90	12.92
3.68	3.76	7.17	7.23						

¹ Average.

At the conclusion of the report the president called for papers relating to the estimation of nitrogen. The following were presented.

THE DETERMINATION OF NITRIC NITROGEN.

By H. C. SHERMAN.

In the hands of the writer the Ulsch-Street method for nitric nitrogen in mixed fertilizers is both more rapid and more accurate than the zinc-iron method. The caustic soda used in the latter method converts some of the organic nitrogen into ammonia during the distillation, and considerable attention is necessary to prevent the soda itself being carried over mechanically.

In working with the Ulsch-Street method, I used 2 grams reduced iron, 10 cc sulfuric acid (1.35 sp. gr.), and 5 grams of magnesia (instead of 3 grams, as directed by the reporter). I always distilled nearly to dryness, or until the content of the flask was reduced to about 30 cc, irrespective of the length of time required. A sample boiled gently for forty minutes, so that about two-thirds of the liquid was distilled, yielded only about two-thirds of its ammonia. I think the low results which have often been obtained by this method are probably due to insufficient distillation.

I have tried this method, carried out as just described, on a few samples of known composition with the following results:

Nitric nitrogen in mixed fertilizers of known composition.

No.	Description of sample.	Calculated.	Found.
		<i>Per cent.</i>	<i>Per cent.</i>
1	NaNO ₃ , (NH ₄) ₂ SO ₄ , KCl, acid phosphate	6.47	6.40
2	NaNO ₃ , bone phosphate, dried blood, ammonite	3.14	3.14
3	NaNO ₃ , tobacco stems, cotton-seed meal, castor pomace.....	5.29	5.26
4	Reporter's sample, 1893	3.46	3.36
5	Reporter's sample, 1894	1.91	1.84
	Average.....	4.05	4.00

These samples, although few, represent the greatest variety of fertilizing materials, and, in view of the high percentages of nitric nitrogen, the results are certainly very satisfactory.

THE AVAILABILITY OF ORGANIC NITROGEN IN MIXED FERTILIZERS.

By S. H. T. HAYES.

Agriculturally considered, the nitrogen question is an important one, for its presence and nature in the soil probably influences more than any other ingredient of plant food the fertility of the soil. That particular phase of the subject, its availability for plant use, is coming to receive more attention as the importance of it is better understood.

Nitrogen is not only the most expensive element in a complete fertilizer, but it comes from a large number of sources, animal and vegetable, and its value in these different materials enjoys an equally wide range. Hence, the necessity of a method for determining the agricultural value of this element, especially in such cases as in the analysis of a mixed fertilizer when the identity of the organic material supplying it is lost. This demand applies only to organic material. Nitrogen present as nitrates or ammonia salts may readily be detected and estimated by existing methods.

Together with this variation in value, ranging between zero in raw leather and 16½ cents in blood, meat, fish, etc., is the rapidly increasing trade in commercial fertilizers, which during the last decade is estimated to have doubled, and which must continue as the virgin fertility of the soil decreases and as the population multiplies. The demand is therefore urgent, if justice is to be done to consumer and

manufacturer, that a method be perfected without delay, combining, if possible, rapidity, simplicity, and accuracy, which shall indicate within reasonable limits the availability of organic nitrogen in fertilizers. It is all the more important when we take into consideration the present system of rating all organic nitrogen as found in a fertilizer analysis as of the highest grade.

DESCRIPTION OF MATERIALS USED IN EXPERIMENTS.

Leather meal.—Preparation not known. It had been roasted, steamed, or otherwise treated, rendering about half of it brittle enough to be easily pulverized, the remainder having the fibrous texture characteristic of ground, raw leather.

Hoof and horn meal.—Was fine, and pulverized to an impalpable powder quite readily.

Cotton-seed meal.—Yellow and nice looking; 6.9 per cent nitrogen.

Castor pomace.—Contained 4.7 per cent nitrogen.

Dried blood.—Pulverized with difficulty; 13.66 per cent nitrogen.

Raw leather.—Ground sole leather scrap.

All material ground to pass 1 mm. mesh sieve, except leather.

FRACTIONAL TREATMENT WITH SULFURIC ACID.

Thus far the pepsin digestion and putrefactive method have been the only ones used in the laboratory for attempting to determine the approximate amount of nitrogen available in organic substances used as fertilizer. Both methods, especially putrefaction, consume much time, besides failing with certain classes of material to give anything like true indications. The value of a method that shall combine simplicity, brevity, and accuracy is therefore obvious.

The destructive (oxidizing) effect of sulfuric acid upon organic material, with the consequent production of ammonia, suggested the possibility of the effect of weaker acid solutions acting for a given time indicating something as to the availability of the nitrogen for plant use, determining the amount of nitrogen evolved. Accordingly, tried the effect of boiling 1 gram of the various kinds of material in 20 cc of 1 per cent, 10 per cent, and 20 per cent solution of H_2SO_4 for five and ten minutes. Owing to a strong tendency to bump while boiling and inability to insure constant flame in each case, resorted finally to steam boiling on water bath, increasing time of treatment. The influence of digesting in pure water was also determined.

Tabulated results showing per cent of total nitrogen evolved are as follows:

	Leather meal.	Ground tank-age.	Hoof and horn meal.	Cotton-seed meal.	Dry ground fish.	Castor pomace.	Dried blood.
	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>
Total nitrogen	7.20	7.21	15.12	6.90	8.91	4.70	13.66
Boiled 5 minutes in 20 cc 10 per cent H_2SO_4	3.69	5.82	6.48	10.00	5.90	8.32	3.72
Boiled 10 minutes in 20 cc 10 per cent acid..	3.53	8.73	8.96	8.11	4.17
Boiled 5 minutes in 20 cc 20 per cent acid ..	3.99	7.71	10.10	10.16	8.10	6.04
Boiled 10 minutes in 20 cc 1 per cent acid..	2.83	5.43	4.67	4.09	4.00	7.52	3.28
Boiled 20 minutes in 20 cc 1 per cent acid..	3.96	5.55	5.97	6.89	5.41	5.02
Steam heated 2 hours in 20 cc H_2O	1.09	3.62	3.01	3.76	2.8735
Steam heated 2 hours in 20 cc 1 per cent acid.....	4.04	6.60	6.32	8.57	6.16	4.66
Steam heated 4 hours in 20 cc 1 per cent acid	3.97	7.87	10.38	5.24
Steam heated 2 hours in 1 per cent acid N in NH_3 in solution determined by Nessler test	5.71	3.97	8.34	5.08	1.99

Solutions were filtered at close of digestion, and nitrogen determined in filtrate by usual method of distilling from alkaline (NaOH) solution.

The indifference manifested on the part of dried blood in these treatments was quite noticeable, in several instances the results being scarcely above those of leather, although compared with results obtained with plants on the same materials not so remarkable.

Digesting in pure water gave rise to a more considerable evolution of ammonia than was anticipated, results not differing much, however, in relation to each other, except in dried blood, from those obtained from weak acid under some conditions. Hydrolysis by water or weak acid is probably the first stage in rendering organic nitrogen available in the soil.

To determine whether all the nitrogen found by distilling filtrate from alkaline solution was in the form of NH_3 at the beginning of distillation made by using Nessler reagent. The results given in the determination of NH_3 show smaller amounts (.2-2.67) in each instance, except with leather. The considerable variations are doubtless due to difficulty in diluting to necessary extent and preserving a representative mixture.

To determine the action of H_2SO_4 on pure albumen, treated egg albumen with 1 per cent and 10 per cent acid, with the following results:

Total nitrogen.....	per cent...	1.85.
Steam heated one hour in 20 cc acid.....	do.....	8.92 of total nitrogen.
Steam heated one hour in 20 cc 10 per cent acid.....	do.....	11.20 of total nitrogen.

DIGESTIONS IN BARIUM HYDROXID $\text{Ba}(\text{OH})_2$.

In studying the decomposition products resulting from treatment of the proteids with various reagents, O. Nasse, and subsequently Schutzenberger, found among a large number of other products that ammonia was produced in varying quantities according to the material.

To determine whether the amount of ammonia set free by treatment with this reagent would to any marked degree indicate the agricultural value of the material as treated, subjected 1 gram each of leather meal, hoof and horn, cotton seed, and dried blood to digestion for one hour in 100 cc of a saturated solution of $\text{Ba}(\text{OH})_2$ in a distilling flask over low flame. The flask was connected with a condenser and standard acid, that no loss of NH_3 might occur during digestion. After digesting, boiling for an hour over low flames, the heat was increased, half the solution distilled off, and the per cent of total nitrogen of the material determined from content in standard acid.

Following are the results of preliminary treatments which did not seem to justify further investigation:

	Leather meal.	Hoof and horn meal.	Cotton-seed meal.	Dried blood.
	Per cent.	Per cent.	Per cent.	Per cent.
Total nitrogen.....	7.20	15.12	6.90	13.66
Boiled two hours in 100 cc $\text{Ba}(\text{OH})_2$	2.64	7.46	7.68	3.07

PEPSIN DIGESTION OF MATERIAL UNDER CONSIDERATION.

By way of check on results made, pepsin digestions of the different materials, as the results of a carefully conducted series of experiments at the Connecticut Experi-

ment Station, show that the availability of nitrogen is quite satisfactorily indicated by the amount digested in pepsin solution in most cases:

	Leather meal.	Ground tank-age.	Hoof and horn meal.	Cotton-seed meal.	Dry ground fish.	Castor pom-ace.	Dried blood.	Raw hoof meal.
	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>
Total nitrogen.....	7.20	7.21	15.12	6.90	8.91	4.79	13.66	14.30
Percent of total nitrogen digested by pepsin.....	58.10	86.34	32.08	82.28	89.03	87.77	97.47	60.37

The above results do not differ materially from those found by others on the same kind of material, except in case of the leather, the mechanical condition of which showed effect of some vigorous treatment in preparation, and raw hoof meal, with which there were no figures to compare.

DIGESTIONS IN KMnO_4 SOLUTIONS.

In accordance with an idea suggested by the analysis of water, using an alkaline potassium permanganate solution to convert albuminoid nitrogen into free ammonia, subjected a gram of material of the different types—leather, cotton seed, hoof and horn, and dried blood—to digestion under similar conditions to those used in $\text{Ba}(\text{OH})_2$ treatment (flask connected with condenser and receiver containing standard acid). The yield of ammonia was considerably greater than obtained with baryta water, but the relation little changed.

Used same amount of solution as above (100 cc), leaving out the potassium hydroxid (8 grams of KMnO_4 per liter), which had the effect of relatively increasing the yield of NH_3 from dried blood, also raising the per cent of yield of cotton seed's nitrogen above that of hoof and horn.

Increasing the amount of KMnO_4 to 16 grams per liter, and using such quantities of material as represented practically the same content of nitrogen (1 gram cotton-seed meal as standard), gave results on which to base hopes for the possible solution of the problem in hand; bone dust, however, giving far higher results than are warranted by the vegetation tests, while leather, having a pepsin digestion coefficient of 38, is below raw leather. It is evident that considerable work has yet to be done on the subject, possibly only to find that the above method or some modification of it has failings equally as objectionable as those of the pepsin method. The simplicity of the method is much in its favor. Also made digestions as above in the acid permanganate solution (10 per cent H_2SO_4 , 8 grams KMnO_4 per liter).

	Leather meal.	Ground tank-age.	Hoof and horn meal.	Cotton-seed meal.	Dried ground fish.	Castor pom-ace.	Dried blood.	Raw hoof meal.	Bone dust.	Raw leather.
	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>Per ct.</i>
Boiled 1 hour in 100 cc alkaline permanganate	13.58	28.69	24.17	18.13
Boiled 1 hour in 100 cc neutral permanganate	1.98	5.02	6.01	4.74
Boiled 1 hour in acid KMnO_4	15.82	11.21	10.20	14.03
Boiled 1 hour in KMnO_4 solution, 16 grams per liter	3.12	13.41	11.39	8.87	9.47	11.80	11.53	14.56	16.37	3.59

Equal amounts of material to equal quantities of nitrogen, cotton seed as standard.

The difference between treating equal amounts of material and equal quantities of nitrogen is also brought out in digesting raw hoof meal in KMnO_4 solution.

	Hoof and horn meal.	Raw hoof meal.
	<i>Per cent.</i>	<i>Per cent.</i>
One gram of material digested.....	7.46	8.77
Half gram digested.....	9.87	14.56

The necessity of treating approximately equal amounts of nitrogen, and not of total material, is therefore apparent.

In conclusion, it may be said that of the various methods tried the digesting in KMnO_4 solution gives most encouragement. Whether, if it is in some way modified, it can be made useful, has yet to be proven by comparisons with plant tests on the same material.

The association adjourned to meet at 9.30 a. m. Saturday.

THIRD DAY.

SATURDAY—MORNING SESSION.

The meeting was called to order at 9.30 o'clock with the president in the chair.

The president called for the report of the committee on recommendations for soil analysis.

Mr. LINDSEY. The committee recommends the Goss method as an alternate method of determining phosphoric acid in soils. The principle is that the soil is boiled about an hour in sulfuric acid with a little mercury. The maximum solubility of phosphoric acid is secured in that time.

The PRESIDENT. What is the objection to changing that to the term adopted by the committee, "optional method?"

After some discussion, the recommendation of the committee was adopted.

Mr. LINDSEY. The method for total nitrogen reads at present, "is determined by the Kjeldahl method, modified to include nitrates, as described in the methods for determining nitrogen, using 14 grams of soil," etc. The recommendation is to modify it to read, "as described in the methods for determining nitrogen, using from 7 to 14 grams of soil except in cases of muck or peat soils."

Mr. BROWN. In the method for the determination of nitrogen in the soil it has been found that the amount of sulfuric acid prescribed is not enough. The amount of acid mentioned will hardly moisten 14 grams of soil, and in order to boil the soil with sulfuric acid considerably more acid must be added.

Mr. Frear indorsed the opinion of Mr. Brown that the quantity of acid was entirely too small, but he would like to insert, for the benefit of inexperienced analysts, a suggestion, that in the case of peat or muck soils smaller quantities of material might be used.

Mr. LINDSEY. That was considered by the committee; but we thought if a person was not competent enough to know that, he had better not do soil analyses.

Mr. GOSS. I agree with Mr. Brown. As the matter stands, there is too much soil and too little acid.

The PRESIDENT. I think possibly a part of this discussion might be settled by the committee to edit this material.

Mr. WILEY. I don't think the analyst ought to be restricted in regard to the amount of soil nor the amount of sulfuric acid. The one depends on the content of nitrogen and the other on the amount of soil subjected to moist combustion.

After some further discussion, Mr. Frear moved to amend the recommendation of the committee so as to strike out all the first sentence of paragraph 13, after the word "nitrogen," on the second line.

The motion as amended was carried.

Mr. LINDSEY. On page 391, No. 2 reads "from 50 to 100 cc of solution A are neutralized," etc. We would like to insert after "A" the words "after the addition of enough ferric chlorid to combine with the phosphoric acid present."

The recommendation was adopted.

Mr. LINDSEY. On page 390, under analysis of ash, where it reads "the residue is moistened with from 2 to 3 cc of hydrochloric acid," we recommend that it be changed to read, "from 5 to 10 cc of hydrochloric acid."

Mr. BROWN. I attempted to analyze the ash this year sent out by the association by the method given, and I found that it would not work.

I think the whole method of ash analysis needs to be looked over and revised. It ought not to be printed as it is without revision. All ashes do not contain more phosphoric acid than can be precipitated. It is necessary to specify what kind of ash analysis. I think it hardly possible to give one method for the analysis of ash to govern all cases. The quantity of hydrochloric acid is a matter of detail. Something should be left to the judgment of the chemist. If 5 cc won't do, use 10; and if 10 won't do, use 20.

Mr. WHEELER. If there is anything wrong, it appears that the committee on revision of methods has power to make it right.

Mr. GOSS. Merely as a matter of information, I would like Mr. Brown to state the points that are wrong.

Mr. BROWN. It would take too much time to state all my reasons here, but I will go over the whole matter with Mr. Goss at another time.

Mr. Myers agreed with Mr. Wiley in thinking it unwise to prescribe exact quantities in case of soil analysis.

The recommendation of the committee was then voted upon and carried.

Mr. LINDSEY. I would state as a committee that we recognize what Mr. Whitney has said with reference to the examination of the physical properties of soil, and under the circumstances do not think it advisa-

ble to give this over to any special reporter, but we do suggest it for the consideration of the association.

The PRESIDENT. I assume that this goes to the association directly as a suggestion and requires no further formal action. We all recognize the importance of Mr. Whitney's work and we are all interested in it. The next thing is the report of the recommendations on phosphoric acid.

Mr. LINDSEY. On page 342, just above "citrate-insoluble phosphoric acid," it is recommended that it be changed to read, "filter, wash with 2.5 per cent ammonia until free of chlorids, burn to whiteness or gray white, and weigh."

The recommendation was adopted.

Mr. LINDSEY. It is recommended that the volumetric method, as described by Mr. Kilgore, be made an alternate or optional method.

Mr. FREAR. I recognize the very careful work which Mr. Kilgore has put upon this method and his success in making it a practical working method; but, as fertilizer chemists, we have a method which is satisfactory and from which this method has a constant tendency to depart. The departure is not great, but still it seems to be quite constant in a given direction. It is possible that the volumetric method is more nearly correct than the gravimetric, and yet the difference is not in most cases a large one. If the method had been tried in any large fraction of the fertilizer laboratories of the country and with as uniform success as it has obtained in three or four, I should unquestionably favor this motion, but I feel compelled, by the pressure which is put upon me at home, to be conservative, and I should very much like to see the method fully stated in the list of methods as recommended for use as a check, but I do not feel that I can vote for it as one to be used in combination with the present official method in the official analysis of fertilizers, or that upon which principal reliance is to be placed, until it has had a wider test than it has had. I think one more year will prove it one which can be adopted as probably the method which we shall use chiefly, because of the great economy in time. But until we have had this test I feel I must vote in the negative on this proposition. I believe it a good method, but I do not think we have had enough evidence to warrant us in placing it in the position which the recommendation would give to it.

Mr. LINDSEY. Your committee hesitated about putting in this recommendation, but we did so on this ground, that I was told that a year ago the committee then acting went over the method carefully and were satisfied that it was worthy of being placed with the official method; but they said, for the sake of being careful, that it should be given another year's trial. It has been given a second year's trial, and has proved as good as a year ago. We recommend it as a whole as an optional method, although, if the association does not wish to adopt it, it might be recommended as a check method.

Mr. WHEELER. I think it would be well for Mr. Kilgore to state what materials it has been tested with, and give a summary of the results

for the two years. The committee last year spent, I think, two or three hours in going over all the results, and were convinced that the results were excellent, and from the work of last year it deserves to be put with the official method, but it is wise to try it at least one year more before its adoption.

Mr. BARTLETT. The results have been good, but many of us have not had opportunity to try the method, and probably if it is made an official method it will be worked a good deal the next year, beside the other official methods, as a test. I think it would be well to give it a trial in that way. I think that is the best test that can be given.

Mr. KILGORE. In reply to Mr. Bartlett, I think he means he has had an opportunity to test it, but has not tested it. I sent Mr. Bartlett a set of samples. I am sure that every chemist of the agricultural colleges and experiment stations, together with commercial chemists, were given an opportunity of taking samples. I sent out forty-five sets, so there was no lack of opportunity for testing the method. With reference to the recommendation, I hesitated myself at first to make it as an alternate method, because the method as originally described by Pemberton is different from the way it was worked this year. I have put a great deal of time on it, and have practically changed the whole of the method. Really all that remains is the strength of the standard solution as given by him. The temperature of precipitation, the molybdate solution, and the method of washing have all been changed. We have used it all this year in our laboratory with the utmost success. We have made many checks on it with materials coming into our laboratory in regular fertilizer work, and we have not a single result that we are not willing to use. They have all agreed well with the official method, though usually lower, which I consider favorable. With reference to the results at the Maryland Station, I will say that eighty determinations were made side by side, and it has been found satisfactory. It has also been tried on reporters' samples for the past three years. I do not wish to present this method to the association as an alternate method if they do not desire it. In our laboratory we have perfect confidence in it, and would like very much to use it in our official work next year. It means a saving of half the time on phosphoric acid, which would dispense with one chemist in the fertilizer work.

Mr. FREAR. I move that the recommendation of the committee be amended as follows: "That the Pemberton-Kilgore volumetric method be recommended as a check method to be tested by official chemists with reference to its adoption next year as an official method."

Mr. KILGORE. I would like to say that this method is not obligatory on anyone. We have an alternate method for potash and nitrogen, but we have no check method for phosphoric acid. In adopting this method as an alternate method, it would still leave the gravimetric method as the principal one. A man need not use it unless he chooses.

Mr. WHEELER. I don't think any of us want to adopt a method we are

not sure is going to give good results with all classes of materials. The proposed amendment is a most excellent one, and will give an opportunity to test the method.

The PRESIDENT. Before taking a vote, I would like to have an expression as to where we stand in regard to section 7 of the constitution. As I understand it, there is presented to the meeting a proposition to adopt a certain method as an optional method, which in my understanding means precisely that it will be equally important with the one we now have. If it is optional, it ought to be as good as the other one. I further understand we have not had the method in the form now proposed until now, as a body. It was not proposed in the form with its modified wash solution, etc., last year. I would like to have an expression as to whether, according to the meaning of section 7, the method has ever been formally presented and an opportunity given to test it in the sense used.

Mr. FREAR. I move it be indicated that the method under consideration has not been presented to the association as required by the clause in the constitution.

Mr. Kilgore stated that opportunity to test the method had been given through the reporter.

Mr. LINDSEY. From the fact that this method has been brought before the meeting, members of the association will understand that opportunity is given to test it and satisfy themselves. Next year it can be voted upon.

The PRESIDENT. The question that is bothering me is, Has the proper opportunity been given?

Mr. KILGORE. I have answered that. The association refuses to bind a reporter, and we can get it in no other way.

Mr. H. B. McDONNELL. Opportunity has already been given to test the method. It has been before us for two years in one form or another. A few of the members do not care to test it, but others ought to be allowed to use it.

Mr. WHEELER. I claim that no proposed change for that method has heretofore been made; and until it has been made, no official opportunity has been given to test it. The opportunity is given as soon as it is published in the proceedings.

Mr. H. B. McDONNELL. The method, as printed by the reporter and sent out in printed form, is just as official as in the Bulletin.

Mr. Ross thought that no radical change had been made in the method; that it was practically the same as last year.

Mr. PATTERSON. It is not a change, but an adoption. I don't like the word "check" as placed in the amendment. I don't think a volumetric method can be considered a check method. It should be considered as a proposed official method, rather than a check method.

Mr. GAINES. I hope it will be published in the proceedings.

Mr. H. B. McDONNELL. In recommending it as an optional method, we only ask that those who want to use it may be allowed to do so.

Mr. PETER. The method has been considered individually; it has been considered by the committee appointed for the consideration of recommendations, and they deem it worthy of trial. I propose the adoption of it as an optional method. It compels no one to use it, and allows those who find it successful to use it in their work.

Mr. FREAR. I think we need to take care in the listing of our methods alternate or optional. After the volumetric method has had a wider test, then we can list it as an alternate method, and if it prove as good as it promises, we will use it for an official method and drop the gravimetric. I object to listing it as an alternate method.

Mr. WHEELER. I believe the question of the adoption of this method is out of order. The method is proposed, and the only thing that can be done is to lay it on the table.

The president stated that they had the recommendation of the committee, and asked for a vote on the amendment proposed by Mr. Frear.

The amendment was lost.

The PRESIDENT. The question now is on the original motion that this method be made an optional method.

Mr. WHEELER. The motion is out of order, and the matter can only be laid on the table.

The PRESIDENT. The chair rules that the vote on the recommendation of the committee is in order, and we will proceed to vote.

Mr. WHEELER. I appeal from the decision of the chair.

Mr. BIGELOW read section 7 of the constitution, and then asked how it was possible to get unanimous consent unless the motion was put before the house.

Section 7 of the constitution is as follows:

No changes shall be made in the methods of fertilizer analyses, except by unanimous consent, until an opportunity shall have been given all official chemists having charge of fertilizer work to test the proposed changes.

Mr. WHEELER. I withdraw my appeal.

After some further discussion, Mr. Van Slyke moved that the method be published with the regular methods under the heading "Provisional volumetric method, proposed for adoption at the next meeting."

The motion was carried.

Mr. LINDSEY. The committee recommends that the association suggest to the reporter the trial of the alkaline citrate-magnesia method, as suggested by Mr. Wiley.

Recommendation adopted.

The president then asked for the recommendations of the reporter on nitrogen.

Mr. Bartlett read the recommendations, as follows:

1. That the Ulsch method be adopted as an official method for determining nitric nitrogen.

2. That, if the association desires it, the zinc-iron method be adopted as an alternate method.

3. That the association adopt the method for determining ammonia with magnesia.

I suggest that the reporter of next year request the members of the association engaged in fertilizer work to give the Fassbender method a thorough trial. I am pleased with the method, and if it can be worked in the cold it will be a great saving of time on fertilizers containing nitrates.

Mr. HUSTON. The next thing in order is the report on dairy products.

REPORT ON DAIRY PRODUCTS.

By E. H. FARRINGTON.

The reporter on dairy products sent, in March, 1895, the following circular to over fifty chemists:

DEAR SIR: Thorough scientific investigation is very much needed in many of the chemical methods now used for the analysis of dairy products. There are also many opportunities for original work in the way of increasing our knowledge of the exact composition of these substances.

Nearly every chemist has some foggy ideas in regard to a particular point in the composition or method of analysis of either milk, butter, or cheese, and is undoubtedly anxious for an opportunity to obtain some clarifying evidence.

The annual reports of this association are now extensively circulated and consulted. They afford an opportunity for publishing the worthy results of investigations, and the value of the dairy products report in the 1895 publication will depend entirely on the chemists' contributions.

It is your reporter's opinion that more and better work may be done if each chemist will send to him, on or before August 1, 1895, a report on some work of his own selection, rather than for me to attempt to supply samples and directions for investigations.

The following suggestions for work have been received by your reporter:

Cheese analysis:

- | | | |
|---|---|--|
| I. Fat..... | { | 1. By the Babcock test.
2. By drying at 100° C. and extracting.
3. By provisional method adopted.
4. By modification of provisional method adopted. |
| II. Determination of acid in cheese. | | |
| III. Determination of different classes of nitrogen compound. | | |

The determination of albuminoids in milk:

- I. What is the correct factor for casein and albumen?
- II. Does Ritthausen's method precipitate all the albuminoids, and in a state of purity?
- III. How are casein and albumen best determined separately?
- IV. What is the amount of nonalbuminoid nitrogen in milk?

The value of this annual report on dairy products depends on the chemists' reporting or failing to report.

E. H. FARRINGTON,
Reporter on Dairy Products.

MADISON, WIS., March, 1895.

In response to this circular your reporter has received one communication, which is herewith presented:

WISCONSIN AGRICULTURAL EXPERIMENT STATION,
Madison, Wis., August 15, 1895.

Prof. E. H. FARRINGTON,

Reporter on Dairy Products for the Association of Official Agricultural Chemists.

DEAR SIR: The comparative results obtained by official chemists during the past two years, with formula for the calculation of the solids of milk from the specific gravity and per cent of fat, show beyond question that the formula,¹ Solids not fat = $\left(\frac{100 S - FS}{100 - 1.0753 FS} - 1 \right) (100 - F) 2.6$, proposed by me gives figures considerably too high.

¹ Eighth Annual Report, Wisconsin Agricultural Experiment Station.

A recalculation of the constant factor of this formula from the analyses given in the last two reports of the association, combined with data obtained at this station during the past year, gives its value as 2.5 instead of 2.6. With this change the formula becomes: Solids not fat = $\left(\frac{100 S - FS}{100 - 1.0753 FS} - 1 \right) (100 - F) 2.5$, in which form I believe it will in most cases, when applied to normal milks, give results agreeing closely with those obtained by gravimetric analysis.

In this formula it is assumed that the difference between the specific gravity of the milk serum and that of water is directly proportional to the per cent of solids in the serum. This assumption is not true, and might lead to a considerable error if the solids of milk serum were always of the same composition, as in such case the specific gravity of the milk serum and the per cent of solids which it contained would change at different rates. To illustrate: 100 cc of milk serum having a specific gravity of 1.036 and containing 9 per cent of solids would weigh 103.6 grams, and the solid contained in it would weigh 9.324 grams. If this be diluted with 100 cc of water, there would be, as there is practically no change in volume, 200 cc, weighing 203.6 grams. It would still contain 9.324 grams of solids, which is nearly 4.58 per cent. The specific gravity of the resulting liquid would be 1.018, and if the change in per cent of solids had been at the same rate as the change in specific gravity it should have contained only 4.5 per cent of solids, or nearly 0.08 less than the actual. In the same manner it may be shown that for specific gravity above 1.036, or for whatever point the ratio of solids to specific gravity is determined, the per cent of solids in the liquid will be less than would be expected from the change in specific gravity. The error, however, from this source, with normal milks containing from 8 to 10 per cent of solids not fat is small, amounting in no case to as much as 0.05 per cent, and this, I believe, is in most cases offset by changes in the composition of the milk solids. If there is no compensation of this kind the formula should in general give results too low with milks having less than the average per cent of solids in the serum and too high where these solids are above the average. I have not found this to be the case, as in a large number of comparative determinations with milks differing widely in the amount of solids not fat, over 70 per cent of the results obtained have been in the opposite direction. A possible explanation may be found in changes in the relative proportions of sugar and casein in the milk.

For the reason that a given amount of milk sugar increases the specific gravity of milk serum more than an equal amount of casein, it follows that a factor expressing the relation between specific gravity and solids in milk of average composition would not apply to milk where the ratio of casein to sugar differs from the average. In the above formula the factor 2.5 is a trifle too large for milks containing more than the average amount of sugar, compared to casein, and too small where the opposite is true. This is clearly shown by applying the formula to whey, which is milk serum from which the casein has been removed, in which case the per cent of solids obtained is always too high. If, then, a low per cent of serum solids is associated with a relatively high proportion of sugar, the effect would be to change slightly the relation between specific gravity and solids in a direction which would tend to compensate for the error alluded to in this formula. I believe in general that this is true, and that in consequence the formula is more accurate than if based upon the assumption of a constant specific gravity for the solids of the serum. The formula with the constant factor of 2.5 gives almost identical results with that of Hehner and Richmond,¹ viz, $t = \frac{F + .2182 S}{.859}$. If $\frac{S}{t} > 2.5$, correct the value obtained for t by adding $.05 \left(\frac{S}{t} - 2.5 \right)$. It gives lower results than Richmond's new formula,² that was submitted to the last convention, viz, $t = 2.625 \frac{100 S - 100}{S} + 1.2 F$.

Any of the three formulas mentioned in this paper will in most cases give satisfactory results for solids, especially as the error falls entirely upon the solids not fat, where it is of comparatively little importance. There is with all formulas of this nature a possible error, arising from differences in the composition of milk, which render them inapplicable in scientific investigation, especially where the milk of single animals is involved. They will, however, be found of great service in milk inspection, where an error of a few tenths per cent in the solids not fat would not mislead.

During the protracted drought of the present summer the solids not fat have been abnormally low, the average of nearly one hundred determinations in milk received at the University of Wisconsin creamery being but a trifle over 8.5 per cent. The

¹ Analyst, 13-26.

² Proceedings of Eleventh Annual Convention of the Association of Official Agricultural Chemists, p. 181.

calculated solids in these milks have averaged about 0.05 per cent higher than found by gravimetric analysis, and with certain patrons have usually ranged from 0.2 to 0.3 per cent higher. The casein in these milks has been found very low, often falling below 2 per cent, while the sugar has remained about the average. I believe this amply explains the high figures obtained by the formula. This low per cent of casein during droughts is in accordance with results obtained by Dr. Van Slyke in New York, and is amply confirmed by the relatively low yield of cheese in factories in regions which have suffered from drought.

All of the complete formulas proposed for this purpose are necessarily complicated and the calculation tedious without the use of tables. I have accordingly prepared from my formula the appended table giving the per cent of solids not fat corresponding to Quevenne lactometer readings (1,000 sp. gr. — 1,000) from 26 to 36, and for per cents of fat up to 6.

An inspection of this table shows that the per cent of solids not fat increases practically at the rate of 0.25 for each lactometer degree and 0.02 for each tenth per cent of fat. This relation is expressed by the simple expressions: Solids not fat = $\frac{L}{4} + .2F$ and total solids = $\frac{L}{4} + 1.2F$, in which L = Quevenne lactometer reading, and F = per cent of fat. This is identical with the short formula of Hehner and Richmond¹ transposed to express total solids, and by the addition of 0.14 is the same as the short formula of Richmond,² viz, $t = \frac{G}{4} + \frac{6}{5}F + .14$. It gives results which differ not more than 0.04 from those of the complete formula for milks containing up to 6 per cent of fat, and has the advantage that it can be easily and quickly applied.

I trust that the association will continue work in this line in order that values may be obtained for the constants of the formulas that will conform most nearly to average conditions in this country.

Very truly yours,

S. M. BABCOCK.

Table showing per cent of solids not fat in milk corresponding to Quevenne lactometer readings and per cent of fat.

Per cent of fat.	Lactometer reading at 60° F.										
	26.	27.	28.	29.	30.	31.	32.	33.	34.	35.	36.
0.0	6.50	6.75	7.00	7.25	7.50	7.75	8.00	8.25	8.50	8.75	9.00
0.1	6.52	6.77	7.02	7.27	7.52	7.77	8.02	8.27	8.52	8.77	9.02
0.2	6.54	6.79	7.04	7.29	7.54	7.79	8.04	8.29	8.54	8.79	9.04
0.3	6.56	6.81	7.06	7.31	7.56	7.81	8.06	8.31	8.56	8.81	9.06
0.4	6.58	6.83	7.08	7.33	7.58	7.83	8.08	8.33	8.58	8.83	9.08
0.5	6.60	6.85	7.10	7.35	7.60	7.85	8.10	8.35	8.60	8.85	9.10
0.6	6.62	6.87	7.12	7.37	7.62	7.87	8.12	8.37	8.62	8.87	9.12
0.7	6.64	6.89	7.14	7.39	7.64	7.89	8.14	8.39	8.64	8.89	9.14
0.8	6.66	6.91	7.16	7.41	7.66	7.91	8.16	8.41	8.66	8.91	9.16
0.9	6.68	6.93	7.18	7.43	7.68	7.93	8.18	8.43	8.68	8.93	9.18
1.0	6.70	6.95	7.20	7.45	7.70	7.95	8.20	8.45	8.70	8.95	9.20
1.1	6.72	6.97	7.22	7.47	7.72	7.97	8.22	8.47	8.72	8.97	9.22
1.2	6.74	6.99	7.24	7.49	7.74	7.99	8.24	8.49	8.74	8.99	9.24
1.3	6.76	7.01	7.26	7.51	7.76	8.01	8.26	8.51	8.76	9.01	9.26
1.4	6.78	7.03	7.28	7.53	7.78	8.03	8.28	8.53	8.78	9.03	9.28
1.5	6.80	7.05	7.30	7.55	7.80	8.05	8.30	8.55	8.80	9.05	9.30
1.6	6.82	7.07	7.32	7.57	7.82	8.07	8.32	8.57	8.82	9.07	9.32
1.7	6.84	7.09	7.34	7.59	7.84	8.09	8.34	8.59	8.84	9.09	9.34
1.8	6.86	7.11	7.36	7.61	7.86	8.11	8.36	8.61	8.86	9.11	9.37
1.9	6.88	7.13	7.38	7.63	7.88	8.13	8.38	8.63	8.88	9.14	9.39
2.0	6.90	7.15	7.40	7.65	7.90	8.15	8.40	8.66	8.91	9.16	9.41
2.1	6.92	7.17	7.42	7.67	7.92	8.17	8.42	8.68	8.93	9.18	9.43
2.2	6.94	7.19	7.44	7.69	7.94	8.19	8.44	8.70	8.95	9.20	9.45
2.3	6.96	7.21	7.46	7.71	7.96	8.21	8.46	8.72	8.97	9.22	9.47
2.4	6.98	7.23	7.48	7.73	7.98	8.23	9.48	8.74	8.99	9.24	9.49

¹ Analyst, 13, 31.

² Analyst, 20, 57.

Table showing per cent of solids not fat in milk corresponding to Querrenne lactometer readings and per cent of fat—Continued.

Per cent of fat.	Lactometer reading at 69° F.										
	26.	27.	28.	29.	30.	31.	32.	33.	34.	35.	36.
2.5	7.00	7.25	7.50	7.75	8.00	8.25	8.50	8.76	9.01	9.26	9.51
2.6	7.02	7.27	7.52	7.77	8.02	8.27	8.52	8.78	9.03	9.28	9.53
2.7	7.04	7.29	7.54	7.79	8.04	8.29	8.54	8.80	9.05	9.30	9.55
2.8	7.06	7.31	7.56	7.81	8.06	8.31	8.57	8.82	9.07	9.32	9.57
2.9	7.08	7.33	7.58	7.83	8.08	8.33	8.59	8.84	9.09	9.34	9.59
3.0	7.10	7.35	7.60	7.85	8.10	8.36	8.61	8.86	9.11	9.36	9.61
3.1	7.12	7.37	7.62	7.87	8.13	8.38	8.63	8.88	9.13	9.38	9.64
3.2	7.14	7.39	7.64	7.89	8.15	8.40	8.65	8.90	9.15	9.41	9.66
3.3	7.16	7.41	7.66	7.92	8.17	8.42	8.67	8.92	9.18	9.43	9.68
3.4	7.18	7.43	7.69	7.94	8.19	8.44	8.69	8.94	9.20	9.45	9.70
3.5	7.20	7.45	7.71	7.96	8.21	8.46	8.71	8.96	9.22	9.47	9.72
3.6	7.22	7.48	7.73	7.98	8.23	8.48	8.73	8.98	9.24	9.49	9.74
3.7	7.24	7.50	7.75	8.00	8.25	8.50	8.75	9.00	9.26	9.51	9.76
3.8	7.26	7.52	7.77	8.02	8.27	8.52	8.77	9.02	9.28	9.53	9.78
3.9	7.28	7.54	7.79	8.04	8.29	8.54	8.79	9.04	9.30	9.55	9.80
4.0	7.30	7.56	7.81	8.06	8.31	8.56	8.81	9.06	9.32	9.57	9.83
4.1	7.32	7.58	7.83	8.08	8.33	8.58	8.83	9.08	9.34	9.59	9.85
4.2	7.34	7.60	7.85	8.10	8.35	8.60	8.85	9.11	9.36	9.62	9.87
4.3	7.36	7.62	7.87	8.12	8.37	8.62	8.88	9.13	9.38	9.64	9.89
4.4	7.38	7.64	7.89	8.14	8.39	8.64	8.90	9.15	9.40	9.66	9.91
4.5	7.40	7.66	7.91	8.16	8.41	8.66	8.92	9.17	9.42	9.68	9.93
4.6	7.43	7.68	7.93	8.18	8.43	8.68	8.94	9.19	9.44	9.70	9.95
4.7	7.45	7.70	7.95	8.20	8.45	8.70	8.96	9.21	9.46	9.72	9.97
4.8	7.47	7.72	7.97	8.22	8.47	8.72	8.98	9.23	9.48	9.74	9.99
4.9	7.49	7.74	7.99	8.24	8.49	8.74	9.00	9.25	9.50	9.76	10.01
5.0	7.51	7.76	8.01	8.26	8.51	8.76	9.02	9.27	9.52	9.78	10.03
5.1	7.53	7.78	8.03	8.28	8.53	8.79	9.04	9.29	9.54	9.80	10.05
5.2	7.55	7.80	8.05	8.30	8.55	8.81	9.06	9.31	9.56	9.82	10.07
5.3	7.57	7.82	8.07	8.32	8.57	8.83	9.08	9.33	9.58	9.84	10.09
5.4	7.59	7.84	8.09	8.34	8.60	8.85	9.10	9.36	9.61	9.86	10.11
5.5	7.61	7.86	8.11	8.36	8.62	8.87	9.12	9.38	9.63	9.88	10.13
5.6	7.63	7.88	8.13	8.39	8.64	8.89	9.15	9.40	9.65	9.90	10.15
5.7	7.65	7.90	8.15	8.41	8.66	8.91	9.17	9.42	9.67	9.92	10.17
5.8	7.67	7.92	8.17	8.43	8.68	8.94	9.19	9.44	9.69	9.94	10.19
5.9	7.69	7.94	8.20	8.45	8.70	8.96	9.21	9.46	9.71	9.96	10.22
6.0	7.71	7.96	8.22	8.47	8.72	8.98	9.23	9.48	9.73	9.98	10.24

At the conclusion of the report on dairy products the president called for papers relating to that subject. The following paper was presented:

ON THE DETERMINATION OF THE ACIDITY OF MILK AND CREAM.

By C. G. HOPKINS and W. A. POWERS.

As early as 1877 work was reported from Denmark along this line (Tidsskrift for Landökonomi, 1877, p. 569), which showed that sour cream gave a better yield of butter than sweet cream.

Fleischmann (Jahresbericht über die Thätigkeit des Molkerei-Instituts, 1884, and *Milchzeitung*, Jan. 27, 1886) made some quantitative determinations of the acid and decided upon a minimum degree of acidity of cream for the highest yield of butter. Fleischmann's method consisted in diluting the cream with four volumes of water, coagulating the casein by heat, and titrating the filtrate.

In 1885 Sebelien used the same method which is in common use to-day, namely, direct titration with one-tenth normal alkali (caustic potash or soda) with phenolphthalein as an indicator. His results were reported in full in 1887. (*Jour. f. landw. Versuchs-Stationen.*)

In this country this method is popularly known as "Manns' acid test," it having been introduced here by Dr. A. G. Manns about 1890.

Some experimental work confirmatory of the results of Fleischmann and Sebelien was reported by Manns in 1890. (*Bull. No. 9, Agr. Exp. Sta. of Univ. of Ill.*)

As early as 1892 one of the writers analyzed a sample of the standard alkali which was then on the market as "Manns' acid test." The sample was brought in by a dairyman who was at that time putting it to practical use in his dairy work. It was found to be practically a one-tenth normal solution of potassium hydroxid.

In 1894 Professor Farrington (*Bull. 32 and 33, Agr. Exp. Sta., Univ. of Ill.*) devised the method of testing the acidity of cream by the use of tablets which contain a certain definite amount of an alkaline carbonate together with a small amount of phenolphthalein. By the use of these and a graduated cylinder the dairyman is enabled to make his own solution of standard alkali, relying upon the accuracy with which the tablets are manufactured.

In Bulletin No. 38, United States Department of Agriculture, page 117, Dr. Van Slyke gave some experimental data which indicate that the direct titration of milk or cream with a standard alkali does not give accurate results. He tested samples of milk containing different amounts of acid (1) by direct titration, (2) by titration after diluting with about ten volumes of water, (3) by titrating the filtrate after precipitating the casein with known amounts of acetic acid, and (4) by titrating the filtrate after precipitating the casein with magnesium sulphate.

On an average the amount of lactic acid which he found as determined by direct titration was about 8 per cent more than by titration after dilution, 101 per cent more than obtained after using magnesium sulphate, and 164 per cent more than by titration after precipitating casein with a known amount of acetic acid. In one case he obtained more acid after precipitating with magnesium sulphate than after simple dilution, and in another case the curious results of $+0.21$ per cent acid by direct titration and -0.30 per cent acid after using acetic acid.

In commenting on these results, Dr. Van Slyke says: "While I am not prepared yet to say that the removal of casein by the use of magnesium sulphate gives absolutely correct results, I believe it to be more reliable than the method now commonly used."

In view of the fact that the common method of testing milk and cream for acidity is in constant use by dairymen, and as we frequently apply it in our experimental work, it seemed to us highly important that this subject be more thoroughly investigated.

Our first effort was to determine the effect of varying the degree of dilution and of varying the amount of indicator used.

Neutral distilled water was used for diluting and a solution of 1 gram of phenolphthalein in 100 cc of 50 per cent alcohol was used as an indicator. One-tenth of a cubic centimeter of this solution is entirely sufficient for ordinary work in acidimetry, and is probably as much as is ordinarily used in testing milk or cream.

Whole milk was used in this work, 25 cc being taken for each test.

Following are the results obtained:

	Water added.	Indicator used.	Per cent acid, as lactic.
	cc.	cc.	
1.....	0	0.1	0.45
2.....	0	2	.36
3.....	50	2	.33
4.....	100	2	.30
5.....	150	2	.29
6.....	200	2	.28
7.....	250	2	.28
8.....	300	2	.28
1.....	225	0.1	0.36
2.....	225	.2	.33
3.....	225	.3	.32
4.....	225	.4	.32
5.....	225	.5	.31
6.....	225	.6	.30
7.....	225	.8	.30
8.....	225	1.6	.28
9.....	225	2	.28
10.....	225	4	.28

These results confirm those of Dr. Van Slyke, which show that too high results are obtained by direct titration without dilution; and our results prove that not less than 2 cc of a 1 per cent solution of phenolphthalein should be used in 25 cc of milk, even when diluted to 250 cc.

Remembering that carbon dioxid affects the delicacy of phenolphthalein, and that considerable quantities of it are present in milk, especially in milk in which much lactic acid has developed, we determined the effect of diluting with boiling water instead of cold water, and also of boiling the diluted solution for a minute or two.

Another sample of whole milk was used in this work; 25 cc of milk and 2 cc of phenolphthalein were used in each test.

Water added.	Per cent acid, as lactic.
None; cold milk.....	1 = 0.91 2 = .90
225 cc, cold.....	1 = .80 2 = .81
225 cc, boiling.....	1 = .73 2 = .72
225 cc, boiling water and liquid boiled 1 to 2 minutes.....	1 = .63 2 = .62

The "end reaction" was found to be much sharper after driving out the carbon dioxid, and the percentage of lactic acid determined is lowered very appreciably.

The following work was done to determine the influence of magnesium sulphate. A saturated solution of magnesium sulphate was used and the same milk as above—25 cc of milk and 2 cc indicator in each test.

Added.	Per cent acid, as lactic.
225 cc cold water and 25 cc magnesium sulphate.....	1 = 0.80 2 = .81
225 cc boiling water, 25 cc magnesium sulphate, and then boiled one to two minutes....	1 = .62 2 = .63

These are identical with the results obtained above without magnesium sulphate, other conditions being the same.

In order to study the influence of casein upon the determination of lactic acid, we first decided to take milk as nearly free from acid as it could easily be gotten, add to it known amounts of acid, and then determine the total acid present.

Twenty-five cc of milk was found to contain the equivalent of 1.2 cc of one-fifth normal lactic acid. After adding 25 cc of one-fifth normal lactic acid to other 25 cc portions of the same milk, the whole was titrated, keeping the treatment and conditions uniform.

On two tests the results obtained were 26.2 cc and 26.3 cc, respectively, of one-fifth normal solution; $25 \text{ cc} + 1.2 \text{ cc} = 26.2 \text{ cc}$, the amount calculated to be present. These results indicate that the casein has but little, if any, influence upon the titration. If the 1.2 cc were entirely due to the influence of casein, it would still be less than 5 per cent of the total acid.

In this connection, an attempt was made to determine the lactic acid by precipitating the casein with lactic acid, making up to a definite volume, filtering through a dry filter, and titrating a portion of the filtrate corresponding to an aliquot part of the original volume.

Ten cc or 25 cc of milk were taken, the casein precipitated with lactic acid, the liquid diluted to 1,000 cc, and then three portions of 250 cc each separated by filtration. These were titrated separately, and the filter with its contents was put into a beaker together with the remaining 250 cc, and titrated. This contained all of the casein. The filtrates were quite clear. Following are the results:

[Lactic acid, one-fifth normal.]

Milk taken.	First 250 cc filtrate.	Second 250 cc filtrate.	Third 250 cc filtrate.	Fourth 250 cc residue.
	cc.	cc.	cc.	cc.
10 cc.....	5.9	5.9	6	7.8
Do.....	12.2	12.2	12.3	14.1
Do.....	24.6	24.7	24.7	27
25 cc.....	7.8	7.7	7.8	11.1
Do.....	4.9	4.9	4.9	9.9
Do.....	6	5.9	5.9	11.1
Do.....	10.9	10.9	10.9	16.1
Do.....	12	12.2	12.1	17.6

These results plainly indicate that the casein has a certain influence upon the acid. The fourth 250 cc aliquot, which contains all of the casein, retains much more than one-fourth of acid, usually about 5 cc of acid in excess of the other aliquot portions when 25 cc of milk are taken, and about 2 cc of acid when 10 cc of milk are taken, regardless of the amount of acid present. It varies, however, within wide limits.

Plainly, a portion of the filtrate corresponding to an aliquot part of the original volume could not be relied upon in determining the acidity.

We next tried to filter the entire liquid, and to wash the precipitate free from acid. In this work milk was used which showed 1.3 cc one-fifth normal lactic acid. To each of three 25 cc portions of this milk, 25 cc of one-fifth normal lactic acid were added, also 25 cc of a saturated solution of magnesium sulphate, and about 200 cc of boiling water. The solution was filtered. The precipitate was washed, and was then transferred to a mortar and thoroughly rubbed up with water. It was then filtered and washed and again rubbed up in a mortar, and this process was repeated until the washings showed no acid reaction.

Then the filter and precipitate were transferred to a beaker, and the precipitate titrated with standard alkali.

The 1.3 cc acid present in the milk as taken, and the 25 cc acid added, make a total of 26.3 cc.

Following are the results obtained in the tests:

[Lactic acid, one-fifth normal.]

	I.	II.	III.
	cc.	cc.	cc.
First filtrate.....	22.3	22.3	22.1
First washing.....	.7	.6	.2
Second washing.....	.3	.3	.0
Third washing.....	.1	.2
Fourth washing.....	.1	.1
Fifth washing.....	.0	.0
Casein precipitate.....	2.4	2.3	3.4
Total acid found.....	25.9	25.8	25.7
Total acid originally present.....	26.3	26.3	26.3

These totals agree well, considering the long process through which the work was carried; and the results seem to prove conclusively that all of the lactic acid can not be removed from the casein by washing, and that titrating only the filtrate would give too low results, the error being of much greater significance with small amounts than with larger amounts of lactic acid.

Dr. Van Slyke has indicated that similar conditions probably exist when casein is precipitated with acetic acid.

In speaking of a like phenomenon, Dr. Wiley says (Agr. Anal., 2-285): "Many precipitates occlude potash and hold it so firmly that it can not be washed out with hot water, although the potash compounds in the precipitate are perfectly soluble. It appears to be a kind of molecular adhesion."

Our experimental data seem to justify the following statements:

Too high results are obtained (1) by direct titration of milk without dilution, (2) by titration after simply diluting with cold or even with hot water, (3) by titrating with the use of the small quantities of indicator that are ordinarily employed in volumetric work.

Too low results are obtained by precipitating the casein and titrating (1) either an aliquot from the filtrate or (2) the entire filtrate and washings.

The following directions will determine very accurately the amount of acid in milk, giving sharp "end reaction" and uniform results:

Take 20 cc of milk, dilute to about 250 cc with boiling water, and boil for one to two minutes; add about 2 cc of a 1 per cent solution of phenolphthalein and titrate with standard alkali.

Mr. MITCHELL. I thought something could be done at this time toward the formation of a national law on foods and dairy products. I would, however, like some one else to take the initiative.

The PRESIDENT. The matter will be considered in order.

Mr. VAN SLYKE. I move that a committee of three be appointed to consider the matter and report to the association at its next meeting.

The PRESIDENT. Will you specify as to the title under which the committee shall be known?

Mr. VAN SLYKE. Committee on legislation of adulterated foods, or something of that sort.

The PRESIDENT. What is it to include?

Mr. MITCHELL. I think the less we ask for the more likely we are to steer clear of trouble and get what we ask for. We have passed a law this year in our State prohibiting the use of preservatives in dairy products. I think the less we try to do at once in the way of legislation the better for us. If we get a wedge in, we can increase its power.

The PRESIDENT. How much has this committee to consider? How extensive is the field in which it has to work?

Mr. Wiley expressed himself as highly in favor of a national pure-food law, but thought it almost useless to try to secure legislation on the subject, as public sentiment did not demand it.

Mr. Mitchell spoke of the laws they had already passed in the State of Wisconsin, and the benefit derived from them.

Mr. Woods. I believe that matters of this kind should be left to the agricultural colleges or experiment stations, and I move that the whole matter be laid on the table.

The PRESIDENT. The motion has been made and seconded that such a committee be appointed.

Mr. MITCHELL. If Mr. Wiley thinks it will be of no avail, there is no objection in putting ourselves on record.

The PRESIDENT. I think there is a good field for that committee. It can take the matter under consideration and report on the subject. There are numerous ways in which we can be of service, and such a committee can do lots of good without the slightest danger to the association.

Mr. Frear thought the association might do good in that direction without damage to its reputation as a scientific body, and on the whole expressed himself as in favor of the appointment of the committee.

The motion was carried without further discussion.

REPORT ON SUGAR.

By E. E. EWELL.

The only recommendation made by the reporter on this subject last year for our guidance in the work of the present year was that the study of the methods for the determination of moisture be continued. As many of the other official methods under the head of sugar analysis have never been made to yield very satisfactory results when subjected to comparative trials by the members of this association, your reporter regarded it very important that trials of these methods should not be abandoned until they are made to yield more gratifying results. A letter expressing this opinion was sent to the chemists of the various experiment stations. Of the nine chemists who consented to take part in the work only three furnished reports.

As the work of the past has shown how large the discrepancy can be between the results obtained in the analysis of comparatively impure saccharine substances, I thought that, in renewing the work, it would be more encouraging to attempt to find how closely results can be made to agree in the case of purer materials. When we have tested our methods under somewhat favorable circumstances, we shall be better prepared to attack the more complicated problems offered in the analysis of low-grade products. With purer materials it is also very much easier to discover

and eliminate sources of error. As will be pointed out later in this report, I am thoroughly convinced that some of the methods now official can not be otherwise than extremely faulty when applied to very low grade materials.

It has been the experience of previous reporters on this subject that it is rather difficult to prepare samples of saccharine liquids for analyses to be made weeks or months afterwards without danger of fermentation or of the crystallization of a portion of the sucrose contained in them. Profiting by the experience of these gentlemen, the sample was prepared by agitating an excess of commercial yellow sugar with cold water for several hours, and then filtering the saturated solution thus obtained. After thorough mixing, this sirup was placed in bottles, securely corked, and sterilized before shipment to the various analysts.

The following letter of instructions was sent with the samples:

UNITED STATES DEPARTMENT OF AGRICULTURE,
DIVISION OF CHEMISTRY,
Washington, D. C., April 8, 1895.

DEAR SIR: I send you, under separate cover, a sample of sirup for your use in trials of the official methods of the A. O. A. C. for the analysis of such substances. As many chemists will probably not have time to make all of the determinations, it is requested that they be taken up in the order in which they are named below. A comparison will thus be obtained of those methods which are the most troublesome and in greatest need of improvement.

1.—DETERMINATION OF WATER.

Little that is encouraging has been reported in regard to this determination since the last meeting of the association, excepting a preliminary note concerning a modification of Weisberg's pumice-stone method (*Bull. Assoc. Chim. France*, 11, 524; *Proc. 11th Ann. Con. A. O. A. C.*, p. 272), upon which Messrs. Carr and Sanborn, of this laboratory, have been working for several months. It is to be hoped that the extreme conservatism of these gentlemen will permit them to announce their promising modification of this method in detail before the time arrives for the reporter on methods for sugar analysis to send out samples for 1896.

As none of the methods tried last year promised to be better than the present Official one, the persons undertaking the work are asked to use this method (see *Bull. 43*, p. 351). In your report please give detailed data in regard to the time of drying, the loss of weight during each period, and the weight of material taken for the determinations. Also, please briefly describe the construction of the oven used.

If time permits, determine water by means of a pycnometer or by dilution and use of a pycnometer.

2.—DETERMINATION OF SUCROSE.

Make this determination by each of the inversion methods (*a, b, c*, pp. 359 and 360 of *Bull. 43*).

As the method which uses yeast as the inverting agent has become very important for the determination of sucrose in the presence of other carbohydrates, please try this method also. It is to be conducted as follows:

Obtain the polariscopic reading before inversion by the ordinary method. Then, for the reading after inversion, dissolve 13.048 grams of the sample in about 50 cc of water in a 100 cc flask, heat in the water bath to 55°, and add one half cake of compressed yeast, which must be thoroughly disintegrated by shaking. After maintaining the temperature of the mixture at 55° for five hours, add 2 cc of a saturated solution of mercuric chlorid to kill the yeast, cool to the temperature of the room, clarify, filter, and polarize.

The direct and indirect readings should be made at approximately the same temperature, which should be the same as that of the solutions at the time of completing their volume and filtering them. Please report in full, weights taken, volume to which diluted, readings before and after inversion, and temperatures at the time of filling flasks to the mark, as well as at the time of making the polariscopic readings.

If you have time, please determine sucrose by the gravimetric method, using the Clerget, the official German, and yeast methods for making the inversion. Give a detailed account of your method of manipulation and all the figures necessary for repeating the calculations. For this calculation, use the table on page 356, *Bulletin 43*.

3.—INVERT SUGAR.

Use method (d), page 355, Bulletin 43. If sufficient time is at your disposal, make determinations by one or both of the official volumetric methods. Use no lead or other clarifying agent in preparing solutions for the determination of invert sugar.

Very respectfully,

E. E. EWELL,
Reporter on Methods for Sugar Analysis.

As it was hoped to make this work of interest to all persons engaged in the study of carbohydrates in agricultural products, as well as to those directly interested in the sugar industry, a first step in the extension of the applicability of the methods included under the head of "Methods of sugar analysis" was made in the recommendation for trial of a method of inversion of sucrose by means of yeast or the inverting agent contained therein. Unfortunately, your reporter momentarily forgot the use of starch in the preparation of compressed yeast, and directed the use of heat for the sterilization of the mixture after inversion. The rotatory power of the starch, thus rendered soluble, would of course render the method useless. This error may be avoided by the use of mercuric chlorid for the sterilization, but a blank control experiment is still necessary, as the yeast contains soluble optically active substances. [This correction has been made in the letter of instruction as given above.] Moreover, neither the Clerget factor nor the factor used with the official German method is applicable when the inversion is made with yeast, the acid present in the first two methods increasing the rotatory power of invert sugar. The results given under the head of "Yeast method" in the table which follows were obtained by use of the factor 142.66.

The analytical data furnished have been arranged in the following tables, which will be found, for the most part, self-explanatory:

Analyst.	Sucrose.						Reduc- ing sugars.	Total solids.	
	Direct polar- ization.	Optical methods by inversion.				Gravi- metric method.		Spin- dle.	Pyc- nom- eter.
		Official (a).	Official (b).	Official (c).	Yeast method.				
T. L. Lyon, Lincoln, Nebr.	60.2	60.39	60.24 60.27	¹ 60.03	² 57.32	-----	-----	-----	
M. E. Jaffa and Geo. E. Colby, Berkeley, Cal	-----	60.87	-----	-----	-----	60.52	5.00	68.30	
Oma Carr, U. S. Depart- ment of Agriculture	-----	-----	-----	-----	-----	-----	-----	68.29	
Reporter	³ 60.18	60.43	60.29	-----	⁴ 57.21	60.99	4.27	68.18	
	60.15	-----	-----	-----	-----	60.72	4.30	68.25	
							4.23	68.25	
							4.30		

¹ The continued evolution of gas rendered the completing of the volume very difficult.

² Followed instructions exactly, i. e., heated to kill the yeast.

³ Hundredths obtained by correction for error in the volume of the flask used.

⁴ Killed the yeast by use of mercuric chlorid.

The determinations of water by drying, reported by myself, were made for a comparison of the relative values of the pumice-stone method and the official method rather than for an actual determination of water by the latter method. The first weighings were made much sooner (at the end of five hours) than the official method directs. Your reporter feels justified in recommending the abandonment of the present official method in the case of all liquid and semiliquid products. In its place, he recommends the adoption of some form of the pumice-stone method, the drying to be conducted in vacuum in some cases, possibly in all cases, the temperature being increased as the relative stability of the material under examination increases. The first noteworthy mention of this method in chemical literature seems to be in an article on the subject by the French chemist, Weisberg, who recommends the method very highly. This article appeared in March, 1894 (*Bull. Assoc. Chim., France*, 1894, 11, 524). As the method has also been made the subject of an elaborate series of experiments by Messrs. Carr and Sanborn, of the laboratory of the Department of Agriculture, evidence of its value is not wanting.

The following paper on drying organic matter was presented:

THE DEHYDRATION OF VISCOUS ORGANIC LIQUIDS.

By OMA CARR and T. F. SANBORN.

Under this title the authors read, at the seventy-sixth meeting of the Washington section of the American Chemical Society, a preliminary note regarding their work in the elaboration of new and improvement of old methods of moisture determinations in liquids which are unstable under ordinary conditions of drying (*Jour. Am. Chem. Soc.*, V, XVII, 2, Feb., 1895). In that paper a rough outline of the method which promised superior results upon further trial was accompanied by a brief résumé of the results obtained thereby over a wide range of difficult common materials. No mention was made, however, of the many parallel trials with other methods. Results covering such determinations are given without comment in following tables.

DIFFICULTIES OF DEHYDRATION.

It is not deemed necessary to call particular attention to the difficulties of dehydrating organic liquids, because such operation is one of the commonly attempted manipulations of the laboratory. Neither is it considered essential to note the many methods proposed for avoidance of the direct estimation of water, particularly in industrial chemistry applied to sugar and glucose. The difficulties are due in the main to the readily decomposable or oxidizable substances contained in all vegetable juices, and the majority of proposed remedies seek to effect the determination by reference to the specific gravity. For many purposes existing methods suffice; but in the refinements sought in the rigid control of industrial processes, as well as in the accuracy essential in analytical schemes, the conventional methods are far from satisfactory.

The direct methods consist simply in the evaporation of the water from a definite portion of the liquid, differing solely in the manner of procedure. For example, it is found that drying the same quantity of substance during the same time at the same temperature, but in vessels of differing shapes, affords results widely divergent. Further, the addition of a conducting or distributing medium changes the results still further. Conducting the desiccation with regard for the avoidance of oxidation—in an atmosphere of hydrogen or carbonic acid, or, the reverse, in vacuo—gives rise to another series of results. No better illustration of this difference of figures on the same material by different methods of procedure may be quoted than the work of the association.

The difficulty of quantitative dehydration of the class of materials here referred to is due solely to decomposition and oxidation, one causing an apparent excess and

the other a deficit in the final percentage of water. Complete removal of this difficulty may be accomplished in but one way, viz, establishment of the conditions under which decomposition and oxidation may not occur. We may, perhaps, effect this operation by a study of the conditions under which decomposition and oxidation do occur in variable intensity.

EFFECT OF HEAT.

The tendency of many organic materials to undergo decomposition and oxidation at extreme temperatures is very well known. The degree of heat essential to a beginning of these processes is quite established for many organic compounds, a number of quantitative manipulations being based upon accurate knowledge of these changes. Our knowledge of the effect of heat upon the various bodies constituting common sugar products, however, is meager; in fact, we have not been able to frame a method of dehydration in which the extraordinary effects of heat have not rendered it worthless in accurate work.

With the view of demonstrating the effect of prolonged heating at the temperature commonly accepted for the purpose of quantitative dehydration, we prepared two solutions containing practically the same percentage of solids—one of pure sucrose and the other containing sucrose, glucose, sodium chlorid, tannic acid, and gum arabic. These solutions were dried at 100° in an air bath, weighings being made hourly during the period of twenty-four hours' drying. The method employed was as follows:

Clean pumice stone was broken into fine particles the size of No. 4 shot, dust removed, and the particles ignited in a hessian crucible to redness. This material was poured, hot, into flat-bottomed aluminum dishes, and cooled in desiccators. The weight of the dish and stone, covered by a ground plate, having been taken, the solution was thoroughly distributed over the stone by means of a pipette weighing bottle, the weight of solution being found by difference. Future weighings were made quickly, the dish being covered and never touched by the fingers.

The results of this work are embodied in Tables Ia and Ic. By reference thereto it will be seen that the mean of duplicates for pure sugar (Table Ia) showed practically no change during the twenty-four hours, while for the mixture (Table Ic) the decrease was regular after the eighth hour, falling from a maximum of 23.90 to a minimum of 22.18, a difference of 1.81, or about 8 per cent of the theoretical solids. It may be remarked that the percents for the fifth, sixth, seventh, and eighth hours are very close to the theoretical content, but that thereafter the rate of decomposition was rapid and constant.

This conduct was not surprising, being simply another confirmation of the impossibility of submitting certain organic substances to the prolonged effect of the ordinary drying temperature without constant and continuous loss of weight. When we consider that the method employed offered the very best facilities for rapid expulsion of moisture, owing to distribution of small quantities over large surfaces, we may readily comprehend the utter impossibility of securing constant weight in methods where distribution is imperfect and time of drying necessarily longer.

In order to check the preceding results by removing the possibility of oxidation, which might very well proceed simultaneously with decomposition in compensatory measure, the series was duplicated, the only difference of procedure being the substitution of carbonic acid for air as environment. The results are brought together in Tables Ib and Id. Reference to these tabulations will indicate that the behavior of the two solutions was the same as in the preceding series, proving the absence of oxidation in the first.

These results lead readily to the following conclusions:

(1) Prolonged heating of low-grade sugar products at a temperature of 100° in air under atmospheric pressure is accompanied by continuous decomposition or oxidation, the rate of which is dependent upon character of material.

(2) It is impossible to indicate the point of complete dehydration in such materials with certainty, the drying having been accomplished at a temperature of 100° , in air under atmospheric pressure.

It appears to us that the method employed offered superior advantages as regards distribution of the material and rapidity of drying, and every precaution to prevent entrance of error was observed.

EFFECT OF HEAT UPON LEVULOSE.

Inasmuch as sugar products generally, and those of cane-sugar manufacture particularly, contain large percentages of levulose, it is desirable to ascertain the behavior of this sugar under the conditions usually present during dehydration at 100° in air at atmospheric pressure. In this work we employed the material known under the trade name diabetine, which is good commercial levulose. The material was dissolved in water, and the density ascertained by pycnometer at 17.5° . The drying was carried out as in the preceding work in all particulars.

In Table II we have brought together the results of eight hours' drying in quadruplicate. Reference to the table shows an uninterrupted loss from the first to the last hour, when the weighings were discontinued. The per cent of solids decreased steadily from a maximum of 19.02 to 16.90, the solids by pycnometer being 17.75. The range from maximum to minimum during the eight hours was 2.02, or 12 per cent of the theoretical solids. We have platted these figures, and they may be seen in graphic section on the chart.

In addition to the preceding experiments with levulose, similar work was carried out with association sugar sample No. 2, 1894, the solids of which contained 40 per cent levulose. The determinations were made as in the foregoing work, in quadruplicate, weighing hourly. The diluted material was employed, the solids by pycnometer being 25.5, which may be taken to represent true solids inasmuch as the mixture consisted of sucrose and levulose. The range from maximum of 25.9 to 24.5 (Table VI c) amounts to 1.40, or about 6 per cent of the theoretical solids. It may be remarked that for the two, three, four, and five hours the found solids, average of quadruplicates, stood exactly at the per cent indicated by the specific gravity. After the fifth hour, however, the decrease was marked and rapid. These results will also be found platted on the chart.

From these results we may conclude that it is impossible to dehydrate quantitatively solutions containing levulose without the occurrence of decomposition, if the temperature be 100° , the environment, air, and the pressure equal to that of the atmosphere.

INFLUENCE OF REDUCED PRESSURE AND TEMPERATURE.

It appearing from the foregoing experiments that the decomposition found at 100° is simply a function of temperature, we decided to ascertain the effect or effects of lower degrees of heat. This we accomplished by conducting the dehydration in vacuo, maintaining the temperature slightly in excess of the water boiling-point corresponding to the pressure. The first experiment was conducted by weighing the diluted levulose solution upon pumice stone contained in a small, thick-glass flask, connecting this with the vacuum pump, and placing the flask in an air bath. The vacuum was 25 inches, corresponding to a water boiling-point of 57° . The temperature of the bath was kept at 70° —an excess over the boiling point of 13° . The drying was slow, requiring eight hours to reach the neighborhood of the solids indicated by density. At the fourteenth hour the per cent had reached the theoretical solids and remained there until discontinuance of weighings at the end of thirty hours. These figures are to be found in Table III, and have been platted in section on the chart.

The second experiment was conducted in a vacuum oven (fig. 2), designed by one of us for the purpose of facilitating the expulsion of moisture. The diluted levulose solution was weighed upon pumice stone in flat-bottomed dishes as in the previous

experiments, and the drying conducted precisely as heretofore, with the exception regarding lower pressure and temperature, the latter being maintained at 70° , or 13° in excess of the boiling point. The results (Table IV) are quite as extraordinary as in the vacuum experiment given above. The theoretical solids by the pycnometer was 17.10 per cent. At the end of four hours drying, or the first weighing, the mean of triplicates was 17.09, which figure was practically maintained during seventeen hours, or until weighings were discontinued. The widest variation was 0.03 per cent, or 0.17 per cent of the total solids. Compared with the results upon the same material at 100° under atmospheric pressure during one-half the time of submission to heat (the loss in such case being 12 per cent of the total solids), these figures appear remarkable.



FIG. 2.—Vacuum drying oven.

From these experiments we hazard these conclusions:

(1) Levulose does not decompose when dried in vacuo, absolute pressure 5 inches mercury, at 70° .

(2) It is possible to dehydrate levulose solutions without decomposition—that is, to constant weight, at a temperature not exceeding 70° .

In an oven constructed with due regard to the necessity of rapid expulsion of moisture vapor it is possible to reach constant weight, operating as in the foregoing experiment, in at most four hours drying. That this constant weight corresponds to complete dehydration is indicated by the agreement, in the case of levulose, of the solids found by drying and that found by specific gravity. In impure materials

where the specific gravity is useless as an index of the true solids, we are compelled to accept the occurrence of constant weight as the point of complete dehydration, and it appears that this level of weight may be maintained, even on a material so sensitive to the effect of heat as levulose, during long periods—in the two experiments detailed for sixteen and seventeen hours, respectively. How much longer this level might have been held, in the instances cited, may not be stated, but it appears that decomposition does not occur under the conditions employed, and that the level of weight might have been maintained indefinitely.

The association sample of 1895, although containing no levulose, or a very minute quantity, was dried under conditions of vacuum and temperature noted for the levulose experiments above; and the means of quadruplicates, which varied among themselves but 0.03 per cent on the diluted material, stood at a level of 19.74 during six hours, or a total drying period of ten hours. Calculated to the original material, the mean of the quadruplicates is 0.9 higher than the solids indicated by pycnometer and about the same per cent higher than the solids found by drying at 100° under atmospheric pressure and selecting arbitrarily two successive weighings approximately the same. The figures found by the latter method, however, show the continuous decrease mentioned above, the solids per cent being selected arbitrarily and not based upon an actually permanent weight. Judging from results secured upon solutions of known strength, we believe our results upon the 1895 sample more nearly represent true solids than those secured by drying at a temperature and under conditions known to be favorable to decomposition and oxidation, and by the use of which it is impossible to secure a permanent level of weight upon materials known to be subject to decomposition and oxidation. Check determinations in duplicate upon the 1895 sample confirm the previous determinations in quadruplicate. After reaching constant weight in vacuo at 70° (water boiling-point 57°), the dishes were dried sixteen hours in a water-jacketed bath at 100° under atmospheric pressure. The results at 70° in vacuo confirm the determinations in quadruplicate, and are thus stated:

In vacuo at 70°:	{ 4 hours.....	17.28	17.26	69.22	69.14
	{ 6 hours.....	17.28	17.26	69.22	69.14
In air at 100°:	{ 4 hours.....	17.50	17.52	70.00	70.03
	{ 16 hours.....	17.60	17.76	70.40	71.04

It appears from these results that oxidation began immediately upon subjection of the material to a temperature of 100° after previous complete dehydration at a lower temperature.

In conclusion, we desire to say that our conclusions regarding the method to be described in the next paragraph are not based upon a few simple trials, but upon results covering many different methods and conditions. Our work embraces upward of 5,000 separate determinations, ranging over all the better-known methods and covering such materials as pure sugar and levulose solutions, honey, molasses, molasses "flowers," sorghum, beet and maize juices, milk, cream, rosin-turpentine solutions, tanning extracts, etc. Part of this comparative work is represented in the following tables, which are submitted without other than necessary comment.

THE METHOD.

(1) Select clean, fine-grained pumice stone and divide into fragments the size of No. 4 shot. Pass the dust through a 40-mesh sieve and treat separately from the larger particles. Digest hot with 2 per cent sulphuric acid and wash until the last trace of acid disappears from the wash water. Owing to the ready subsidence of the material, the washing may be accomplished rapidly by decantation. After complete washing, place the material, wet, in a hessian crucible and bring to redness in a monitor or other convenient furnace. When complete expulsion of water is assured, place, hot, in a desiccator, or direct into the drying dishes if desired for use immediately. In loading the dishes place a thin layer of the dust over the bottom

of the dish to prevent contact of the material to be dried with the metal; over this layer place the larger particles, nearly filling the dish. If the stone has been well washed with the acid no harm may result from placing the dish and stone over the flame for a moment before placing in the desiccator preparatory to weighing.

(2) If the material to be dried is dense, dilute until the specific gravity is in the neighborhood of 1.08 by dissolving a weighed quantity in a weighed quantity of water. (Alcohol may be substituted in material not precipitable thereby.) Of this, 2 to 3 grams may be distributed over the stone in a dish, the area of which is in the neighborhood of 3 square inches, or 1 gram for each square inch of area. Distribute this material uniformly over the stone by means of a pipette weighing-bottle (weighing direct upon the stone will not answer), ascertaining the weight taken by difference.

(3) Place the dishes in a vacuum oven, in which may be maintained a pressure of not more than 5 inches mercury, absolute. The form of oven is not material so long as the moisture escapes freely by passing a slow current of air (dried) beneath the shelf supporting the dishes. The temperature must be maintained at 70° and the vacuum at 25 inches.

(4) All weighings must be taken when the dish is covered by a ground plate, and the open dish must not be exposed to the air longer than absolutely necessary. Weighings should be made at intervals of two or three hours.

TABLE I a.—*Effect of prolonged drying—pure sugar solution.*

Method.—On pumice stone in flat-bottomed dishes, at 100°, weighed hourly. Dried in air.

Specific gravity, by pycnometer, at 17.5° 1.09953
 Degrees Brix corresponding to above 23.6

Hours.	No. 1.	No. 2.	Means.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
1.....	24.01	23.80	23.91
2.....	23.87	23.80	23.84
3.....	23.80	23.74	23.77
4.....	23.99	23.85	23.87
5.....	23.77	23.70	23.74
6.....	23.92	23.64	23.78
7.....	23.93	23.70	23.82
8.....	23.79	23.63	23.71
9.....	23.88	23.61	23.75
10.....	23.94	23.72	23.83
11.....	24.05	23.73	23.89
12.....	24.13	23.71	23.92
13.....	24.05	23.74	23.90
14.....	24.65	23.75	23.90
15.....	24.05	23.70	23.82
16.....	24.05	23.71	23.83
17.....	24.05	23.68	23.87
18.....	23.95	23.52	23.74
19.....	24.00	23.59	23.80
20.....	24.00	23.60	23.80
21.....	23.98	23.54	23.76
22.....	23.91	23.46	23.69
23.....	23.91	23.47	23.69
24.....	23.99	23.52	23.76
Means	23.97	23.66	23.82

Range, maximum to minimum, 0.31.

TABLE I b.—*Effect of prolonged drying—pure sugar solution.*

Method.—On pumice stone in flat-bottomed dishes, at 100°, weighed hourly. Dried in CO₂.
 Specific gravity, by pycnometer, at 17.5°..... 1.09953
 Degrees Brix corresponding to above..... 23.6

Hours.	No. 1.	No. 2.	Means.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
1.....	23.94	24.00	23.97
2.....	23.80	24.08	23.94
3.....	23.75	23.98	23.91
4.....	23.69	23.68	23.69
5.....	23.62	23.67	23.65
6.....	23.60	23.83	23.72
7.....	23.61	23.86	23.73
8.....	23.53	23.78	23.65
9.....	23.48	23.74	23.61
10.....	23.48	23.85	23.66
11.....	23.49	23.93	23.71
12.....	23.44	23.79	23.62
13.....	23.63	24.00	23.82
14.....	23.43	23.86	23.65
15.....	23.30	23.79	23.55
16.....	23.32	23.82	23.57
17.....	23.32	23.83	23.58
18.....	23.22	23.78	23.50
19.....	23.22	23.76	23.49
20.....	23.22	23.79	23.51
21.....	23.11	23.68	23.40
22.....	22.98	23.61	23.30
23.....	22.98	23.61	23.30
24.....	23.09	23.71	23.40
Means.....	23.43	23.77	23.60
RANGE.			
Maximum to minimum....	0.96	0.47	0.67
Maximum to mean.....	.51	.31	.37
Minimum to mean.....	.45	.16	.30

TABLE I c.—*Effect of prolonged drying—mixed solution.*

Method.—On pumice stone in flat-bottomed dishes, at 100°, weighed hourly. Dried in air. (For composition of this solution, see Table VIII.)

Specific gravity, by pycnometer, at 17.5°..... 1.10218
 Degrees Brix corresponding to above..... 24.15
 Degrees Brix, theoretical..... 23.63

Hours.	No. 1.	No. 2.	Means.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
1.....	23.87	23.93	23.90
2.....	23.76	23.67	23.72
3.....	23.72	23.66	23.69
4.....	23.99	23.93	23.92
5.....	23.70	23.72	23.71
6.....	23.65	23.65	23.65
7.....	23.70	23.68	23.69
8.....	23.63	23.64	23.63
9.....	23.47	23.49	23.48
10.....	23.40	23.49	23.44
11.....	23.39	23.42	23.41
12.....	23.37	23.26	23.32
13.....	23.27	23.29	23.28
14.....	23.17	23.24	23.21
15.....	23.06	22.98	23.02
16.....	22.88	22.88	22.88
17.....	22.83	22.83	22.83
18.....	22.55	22.58	22.57
19.....	22.51	22.58	22.55
20.....	22.46	22.49	22.48
21.....	22.38	22.33	22.36
22.....	22.20	22.15	22.18
23.....	22.12	22.09	22.11
24.....	22.20	22.16	22.18
Means	23.13	23.17	23.15
RANGE.			
Maximum to minimum....	1.78	1.84	1.81
Maximum to mean.....	.77	.76	.77
Minimum to mean.....	1.01	1.08	1.04

TABLE I d.—*Effect of prolonged drying—mixed solution.*

Method.—On pumice stone in flat-bottomed dishes, at 100°, weighed hourly. Dried in CO₂. (For composition of this solution, see Table VIII.)

Specific gravity, by pycnometer, at 17.5° 1.10218
 Degrees Brix corresponding to above 24.15
 Degrees Brix, theoretical 23.63

Hours.	No. 1.	No. 1.	Means.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
1.....	23.69	23.96	23.83
2.....	23.76	23.76	23.76
3.....	23.62	23.79	23.71
4.....	23.45	23.66	23.56
5.....	23.26	23.59	23.43
6.....	23.32	23.58	23.45
7.....	23.32	23.58	23.45
8.....	23.11	23.51	23.31
9.....	23.01	23.43	23.22
10.....	22.88	23.41	23.15
11.....	22.82	23.43	23.13
12.....	22.76	23.25	23.01
13.....	22.83	23.29	23.06
14.....	22.65	23.28	22.87
15.....	22.35	22.91	22.63
16.....	22.33	22.80	22.52
17.....	22.15	22.74	22.45
18.....	22.06	22.69	22.38
19.....	21.93	22.69	22.31
20.....	21.86	22.59	22.23
21.....	21.65	22.43	22.04
22.....	21.55	22.34	21.95
23.....	21.44	22.25	22.85
24.....	21.59	22.46	22.03
Means	22.64	23.14	22.89
RANGE.			
Maximum to minimum.....	2.32	1.71	1.88
Maximum to mean.....	1.12	.82	.94
Minimum to mean.....	1.20	.89	.94

TABLE II.—*Solution of diabetine (levulose).*

Method.—On pumice stone in flat-bottomed dishes, at 100°, in air. Weighed hourly for Nos. 1 and 2, and at two-hour intervals for Nos. 3 and 4.

Specific gravity, by pycnometer, at 17.5° 1.07318
 Degrees Brix corresponding to above 17.75

Hours.	No. 1.	No. 2.	No. 3.	No. 4.	Means.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
1.....	18.84	19.19	19.02
2.....	18.49	18.84	18.35	18.42	18.53
3.....	18.39	18.76	18.57
4.....	17.93	18.14	18.23	18.34	18.16
5.....	17.24	17.60	17.42
6.....	16.98	17.44	17.42	17.53	17.34
8.....	17.04	16.92	16.90
Means.....	17.81	18.33	17.76	17.80	17.93
RANGE.					
Maximum to minimum.....	1.86	1.75	1.31	1.50	2.04
Maximum to mean.....	1.03	.86	.59	.62	1.69
Minimum to mean.....	.83	.89	.72	.88	.95

TABLE III.—*Diabetine.*

Method.—On pumice stone in flask connected with vacuum pump, flask being placed in air bath.

Hours.	Temper- ature.	Solids.	H ₂ O.
	<i>Deg. C.</i>	<i>Per cent.</i>	<i>Per cent.</i>
4.....	60	24.91	75.09
8.....	75	15.98	84.02
12.....	75	15.45	84.55
14.....	75	15.17	84.83
16.....	75	15.22	84.78
20.....	65-70	15.30	84.70
23.....	65	15.24	84.76
26.....	60	15.25	84.75
30.....	60	15.25	84.75

Per cent solids, by pycnometer 15.25

Per cent water 84.75

TABLE IV.—*Diabetine.*

Method.—On pumice stone in flat-bottomed dishes, at 70°, in vacuum of 25 inches, in Carr's drying oven.

Solids by pycnometer 17.10

Hours.	No. 1.	No. 2.	No. 3.	Means.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
4.....	17.12	17.09	17.06	17.09
8.....	17.11	17.09	17.08	17.09
12.....	17.06	17.05	17.06	17.06
17.....	17.09	17.07	17.07	17.08

TABLE V.—*A. O. A. C. sample, 1895.*

Method.—On pumice stone in flat-bottomed dishes in vacuum of 25 inches, temperature of 70°, in Carr's drying oven.

Specific gravity of diluted sample, at 17.5° 1.08098
 Degrees Brix corresponding to above 19.49

Hours.	No. 1.	No. 2.	No. 3.	No. 4.	Means.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
2.....	19.85	19.84	19.80	19.80	19.82
4.....	19.76	19.75	19.73	19.73	19.74
6.....	19.76	19.75	19.73	19.73	19.74
8.....	19.76	19.75	19.73	19.73	19.74
10.....	19.76	19.75	19.73	19.73	19.74
Means.....	19.78	19.77	19.76	19.76	19.77

TABLE VI a.—*A. O. A. C. samples, 1894.*

No. 1.

Method.—On pumice stone in flat-bottomed dishes, at 100°, in air.

Specific gravity of diluted sample, at 17.5° 1.09875
 Degrees Brix corresponding to above 23.4

Hours.	No. 1.	No. 2.	No. 3.	No. 4.	Means.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
1.....	23.08	23.09	23.07	23.11	23.09
2.....	22.69	22.78	22.69	22.67	22.71
3.....	22.73	22.78	22.68	22.55	22.69
4.....	22.81	22.73	22.67	22.56	22.69
5.....	22.67	22.74	22.66	22.50	22.64
6.....	22.18	22.17	22.11	21.79	22.06
7.....	21.84	21.91	21.66	21.26	21.67
8.....	21.36	21.50	21.27	20.66	21.13
Means.....	22.42	22.46	22.35	22.14	22.34
RANGE.					
Maximum to minimum...	1.72	1.59	1.80	2.45	1.96
Maximum to mean.....	.66	.63	.72	.97	1.21
Minimum to mean.....	1.06	.96	1.08	1.48	1.21

TABLE VI b.—*A. O. A. C. samples, 1894.*

No. 1.—(See Table VI a.)

Method.—On pumice stone in flat-bottomed dishes, at 100°, in air, weighed at intervals of two hours.

Specific gravity of diluted sample, at 17.5°..... 1.09875
 Degrees Brix corresponding to above..... 23.4

Hours.	No. 1.	No. 2.	No. 3.	Means.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
2.....	22.39	22.49	22.38	22.42
4.....	22.15	22.28	22.26	22.23
6.....	22.26	22.39	22.31	22.32
8.....	22.22	22.36	22.11	22.23
Means	22.26	22.36	22.27	22.30
RANGE.				
Maximum to minimum	0.24	0.21	0.27	0.19
Maximum to mean.....	.13	.13	.11	.12
Minimum to mean.....	.11	.08	.13	.07

TABLE VI c.—*A. O. A. C. samples, 1894.*

No. 2.

Method.—On pumice stone in flat-bottomed dishes, at 100°, in air, weighed hourly.

Specific gravity of diluted sample, at 17.5°..... 1.1085
 Degrees Brix corresponding to above..... 25.5

Hours.	No. 1.	No. 2.	No. 3.	No. 4.	Means.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
1.....	25.64	25.93	25.85	26.17	25.90
2.....	25.43	25.50	25.50	25.51	25.49
3.....	25.42	25.57	25.42	25.57	25.50
4.....	25.41	25.56	25.44	25.60	25.50
5.....	25.52	25.68	25.44	25.56	25.50
6.....	24.97	25.31	24.96	24.99	25.06
7.....	24.78	24.98	24.72	24.77	24.81
8.....	24.53	24.56	24.29	24.61	24.50
Means	25.21	25.38	25.20	25.35	25.29
RANGE.					
Maximum to minimum.....	1.11	1.37	1.56	1.56	1.40
Maximum to mean.....	.43	.55	.65	.82	.61
Minimum to mean.....	.68	.82	.91	.74	.79

TABLE VI d.—*A. O. A. C. samples, 1894.*

No. 2.—(See Table VI c.)

Method.—On pumice stone in flat-bottomed dishes, at 100°, in air, weighed at intervals of two hours.

Specific gravity of diluted sample, at 17.5°..... 1.1085
 Degrees Brix corresponding to above..... 25.5

Hours.	No. 1.	No. 2.	No. 3.	Means.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
2.....	25.48	25.61	25.49	25.53
4.....	25.21	25.52	25.20	25.31
6.....	25.27	25.45	25.33	25.35
8.....	25.45	25.52	25.27	25.41
Means	25.35	25.53	25.32	25.39
RANGE.				
Maximum to minimum	0.27	0.16	0.29	0.22
Maximum to mean.....	.13	.08	.17	.14
Minimum to mean14	.08	.12	.08

TABLE VI e.—*A. O. A. C. samples, 1894.*

No. 2.

Method.—On pumice stone in flat-bottomed dishes, at 100°, in air.

Specific gravity of diluted sample, at 17.5°..... 1.0242
 Degrees Brix corresponding to above..... 6.12

Hours.	No. 1.	No. 2.	No. 3.	Means.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
1.....	6.18	6.31	6.35	6.25
2.....	6.13	6.19	6.19	6.17
3.....	6.09	6.11	6.13	6.12
4.....	6.09	6.15	6.16	6.13
7.....	6.13	6.22	6.21	6.19
Means	6.12	6.20	6.16	6.17
RANGE.				
Maximum to minimum	0.09	0.20	0.12	0.13
Maximum to mean06	.11	.09	.08
Minimum to mean.....	.03	.09	.03	.05

TABLE VII.—*Pure sugar solution.**Method.*—On pumice stone in flat-bottomed dishes, in air, at 100° (a), and in CO₂, at 100° (b).

Specific gravity, by pycnometer, at 17.5°..... 1.09953
 Degrees Brix corresponding to above..... 23.6

Hours.	(a) In air.			(b) In CO ₂ .		
	No. 1.	No. 2.	Means.	No. 1.	No. 2.	Means.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
1½.....	23.71	23.69	23.70	24.43	24.22	24.33
3.....	23.74	23.76	23.75	23.93	23.92	23.93
Means	23.73	23.73	23.73	24.18	24.07	24.13

TABLE VIII.—*Mixed solution.**Composition.*

41.669 grams sucrose.	2.086 grams sodium chlorid.	2.086 grams tannic acid.
4.168 grams glucose.	2.086 grams gum arabic.	Made to a volume of 200 cc.

Method.—On pumice stone in flat-bottomed dishes, in air, at 100°.

Specific gravity, by pycnometer, at 17.5°	1.10218
Degrees Brix, corresponding to above	24.15
Degrees Brix, theoretical	23.63

Hours.	No. 1.	No. 2.	No. 3.	Means.
3.....	23.63	23.70	23.73	23.69

Range:

Maximum to minimum.....	0.10
Maximum to mean.....	.04
Minimum to mean.....	.06

TABLE IX.—*Honey.*

Method.—On pumice stone in flat-bottomed dishes, at 100°. in air.

Specific gravity of diluted honey, at 17.5°	1.0845
Degrees Brix corresponding to above	20.27

Hours.	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.	Means.
	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per cent.</i>
1.....	20.89	20.97	20.82	20.76	20.74	20.83	20.84
2.....	20.66	20.61	20.78	20.52	20.51	20.73	20.64
3.....	20.59	20.62	20.51	20.55	20.52	20.54	20.56
4.....	20.69	20.53	20.60	20.66	20.59	20.67	20.62
Means	20.71	20.68	20.68	20.67	20.59	20.69	20.66
RANGE.							
Maximum to minimum	0.30	0.44	0.31	0.24	0.23	0.29	0.28
Maximum to mean.....	.18	.29	.14	.14	.15	.14	.18
Minimum to mean12	.15	.17	.10	.08	.15	.10

TABLE X.—*Maize juice, 23 years old.*

Method.—On pumice stone in flat-bottomed dishes, at 100°, in air, weighing hourly

Specific gravity, by pycnometer, at 17.5°	1.0655
Degrees Brix corresponding to above.....	16.00
Purity	24.19

Hours.	No. 1.	No. 2.	No. 3.	No. 4.	Means.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
1.....	15.31	15.35	15.24	15.11	15.25
2.....	14.90	15.03	14.98	14.99	14.97
3.....	14.91	15.04	14.94	14.97	14.96
4.....	14.85	14.96	14.85	14.90	14.89
5.....	14.94	14.91	15.00	14.90	14.94
6.....	14.40	14.34	14.46	14.41	14.40
7.....	14.05	14.30	14.34	14.44	14.28
8.....	14.17	14.29	14.43	14.50	14.35
9.....	14.01	14.16	14.38	14.20	14.19
Means.....	14.62	14.71	14.74	14.71	14.70
RANGE.					
Maximum to minimum	1.30	1.19	0.86	0.91	1.06
Maximum to mean.....	.69	.64	.50	.40	.55
Minimum to mean.....	.61	.55	.36	.51	.51

TABLE XI.—*Sorghum juice.*

Method.—On pumice stone in flat-bottomed dishes, at 100°, in air.

Specific gravity by pycnometer, at 17.5°	1.0689
Degrees Brix corresponding to above.....	16.75

Hours.	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.	Means.
	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per cent.</i>
2.....	13.91	13.82	13.80	14.07	13.98	14.02	13.93
3.....	13.65	13.60	13.63	13.80	13.80	13.78	13.71
4.....	13.57	13.50	13.56	13.59	13.62	13.58	13.57
5.....	13.51	13.42	13.45	13.50	13.49	13.43	13.47
6.....	13.41	13.33	13.42	13.34	13.36	13.35	13.37
7.....	13.44	13.35	13.44	13.48	13.46	13.40	13.43
Means.....	13.58	13.50	13.55	13.63	13.62	13.59	13.58
RANGE.							
Maximum to minimum	0.50	0.49*	0.37	0.73	0.62	0.77	0.56
Maximum to mean33	.32	.25	.44	.36	.43	.35
Minimum to mean12	.17	.12	.29	.26	.34	.21

TABLE XII.—*Sorghum juice.**Method.*—On pumice stone in flat-bottomed dishes, at 100°, in air.

Specific gravity by hydrometer, at 17.5°	1.0834
Degrees Brix corresponding to above	20.05

Hours.	No. 1.	No. 2.	No. 3.	No. 4.	Means.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
1.....	18.75	18.73	18.86	18.79	18.78
2.....	18.77	18.65	18.77	18.66	18.71
3.....	18.80	18.86	18.80	18.70	18.79
Means	18.77	18.75	18.81	18.72	18.76
RANGE.					
Maximum to minimum	0.05	0.21	0.09	0.13	0.08
Maximum to mean03	.11	.05	.07	.03
Minimum to mean02	.10	.04	.06	.05

TABLE XIII.—*Cream.**Method.*—On pumice-stone in flat-bottomed dishes, at 100, in air.

Hours.	No. 1.	No. 2.	No. 3.	No. 4.	Means.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
2.....	24.35	24.22	24.47	24.30	24.34
3.....	24.22	24.14	24.19	24.19	24.19
4.....	24.19	24.14	24.19	24.19	24.18
Means	24.25	24.17	24.28	24.23	24.24
RANGE.					
Maximum to minimum	0.16	0.08	0.28	0.11	0.16
Maximum to mean10	.05	.19	.07	.10
Minimum to mean06	.03	.09	.04	.06

TABLE XIV.—*Pure sugar solution.**Method.*—On ignited asbestos-board disks in flat-bottomed dishes, in CO₂, at 100°.

Specific gravity by pycnometer, at 17.5°	1.07751
Degrees Brix corresponding to above	18.7

Hours.	No. 1.	No. 2.	Means.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
2.....	19.95	19.52	19.74
4.....	19.71	19.48	19.60
6.....	19.63	19.52	19.59
8.....	19.45	19.15	19.30
Means	19.69	19.42	19.55
RANGE.			
Maximum to minimum	0.50	0.37	0.44
Maximum to mean26	.10	.19
Minimum to mean24	.27	.25

TABLE XV.—*Mixed solution.*

Method.—On ignited asbestos-board disks in flat-bottomed dishes, in CO_2 , at 100° . (For composition of this solution, see Table III.)

Specific gravity, by pycnometer, at 17.5° 1.0816
 Degrees Brix corresponding to above 19.6

Hours.	No. 1.	No. 2.	Means.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
2.....	18.73	19.00	18.87
4.....	18.48	18.73	18.61
6.....	18.19	17.85	18.02
8.....	17.78	17.67	17.73
Means	18.29	18.31	18.30
RANGE.			
Maximum to minimum.....	0.95	1.33	1.14
Maximum to mean.....	.44	.69	.57
Minimum to mean.....	.51	.64	.57

TABLE XVI.—*Pure sugar solution.*

Method.—Drying in U tube in current of CO_2 , at 100° .

Specific gravity, by pycnometer, at 17.5° 1.07751
 Degrees Brix corresponding to above 18.7

Hours.	No. 1.	No. 2.	No. 3.	Means.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
2.....	18.71	18.43	17.92	18.35
6.....	18.44	18.27	17.72	18.14
Means	18.57	18.35	17.82	18.25

Range, maximum to minimum, 0.75.

TABLE XVII.—*Mixed solution.*

Method.—Drying in U tube in current of CO_2 , at 100° .

Specific gravity, by pycnometer, at 17.5° 1.0816
 Degrees Brix corresponding to above 19.6

Hours.	No. 1.	No. 2.	No. 3.	Means.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
2.....	17.44	17.24	16.93	17.20
6.....	17.17	16.83	16.78	16.93
Means.....	17.31	17.04	16.86	17.06

Range, maximum to minimum, 0.45.

TABLE XVIII.—*Pure sugar solution.*

Method.—Drying in vacuo on Adams's paper (Josse's method), using Spencer's modification of Courtonne's drying oven, at 100°.

Specific gravity, by pycnometer, at 17.5° 1.07751
 Degrees Brix corresponding to above 18.7

Hours.	No. 1.	No. 2.	No. 3.	No. 4.	Means.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
2.....	19.03	17.75	17.70	17.63	18.03
4.....	19.17	17.99	17.52	17.71	18.10
6.....	19.18	18.80	17.75	18.31	18.51
Means	19.13	17.94	17.66	17.88	18.16

Range, maximum to minimum, 1.47.

TABLE XIX.—*Mixed solution.*

Composition:

70.0 grams pure sucrose. 1.3 grams tannic acid.
 10.0 grams sodium chlorid. 10.0 grams gum arabic.
 8.7 grams glucose. Made up to 500 cc.

Method.—Drying in vacuo on Adams's paper (Josse's method), using Spencer's modification of Courtonne's drying oven, at 100°.

Specific gravity, by pycnometer, at 17.5° 1.0816
 Degrees Brix corresponding to above 19.6

Hours.	No. 1.	No. 2.	No. 3.	No. 4.	Means.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
2.....	17.20	19.44	21.94	18.80	19.37
4.....	17.31	19.95	18.42	17.40	18.27
6.....	17.50	17.65	18.27	17.40	17.71
Means	17.33	19.01	19.54	17.87	18.45

Range, maximum to minimum, 2.21.

TABLE XX.—*Molasses "flowers," diluted.*

Method.—Drying in vacuo on Adams's paper (Josse's method), using Spencer's modification of Courtonne's drying oven, at 100°.

Specific gravity, by pycnometer, at 17.5° 1.07889
 Degrees Brix corresponding to above 19.0
 Degrees Brix, by hydrometer, at 17.5° 18.6

Hours.	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.	No. 7.	No. 8.	Means.
	<i>Per. ct.</i>	<i>Per. ct.</i>	<i>Per. ct.</i>	<i>Per. ct.</i>	<i>Per. ct.</i>	<i>Per. ct.</i>	<i>Per. ct.</i>	<i>Per. ct.</i>	<i>Per cent.</i>
2.....	16.97	17.67	16.89	17.58	15.48	17.30	17.60	17.31	17.10
4.....	16.91	17.19	16.86	16.81	14.78	17.23	16.69	17.27	16.72
6.....	16.98	17.11	16.35	16.74	14.75	17.08	16.58	17.12	16.60
Means .	16.95	17.32	16.70	17.04	15.00	17.20	16.96	17.23	16.81

Range, maximum to minimum, 2.32.

The president called for a discussion of the report and papers.

Mr. WILEY. I would like to suggest the importance of drying at low temperatures. In drying levulose at the temperature of boiling water in

the open air, there is a progressive decomposition of the substance, so that the apparent amount of water obtained is much greater than the real percentage of water present. In the drying of honeys, low-grade sugars, and molasses of all kinds, the error is a very important one. It seems to me that the official method should be changed when the proper time comes to include possibilities of that kind. It is easy to dry in a partial vacuum, and it seems to me that all organic liquids, whether viscous or not, and all organic bodies for chemical examination or for the determination of moisture should be dried in a partial vacuum. There would be no danger of oxidation by the proposed method; the drying could be accomplished more regularly and with less danger of injury to the organic substances. Better results could be obtained by adopting a method which would include the good points of all.

The president then called for the recommendations of the reporter on sugar, which were read by Mr. Ewell, as follows:

RECOMMENDATIONS ON SUGAR.

1. That the title of this section of the official methods be changed from "Methods of sugar analysis" to "Methods for the determination of carbohydrates in agricultural products, including methods for the determination of water and ash in commercial and industrial saccharine materials."

2. That the methods for the determination of lactose in milk, as well as other methods which have been adopted, or which shall be adopted in the future, for the determination of carbohydrates in agricultural products, be placed under this head.

3. That the study of the methods thus collected be divided among several reporters, as the association, its executive committee, or its presiding officer may be empowered to determine.

4. That the present official method for the determination of water by drying be abandoned, some form of the pumice-stone method being adopted in its place, provisionally, the drying to be conducted to constant weight either in vacuo or in a water oven.

5. That the third, fourth, and fifth paragraphs, under the head of determination of water, be rearranged and amplified into two paragraphs, with italicized headings, which shall read as follows: One, "Determination of specific gravity, water, and total solids by means of a spindle;" the other, "Determination of specific gravity, water, and total solids by means of a pycnometer."

6. That a complete table for the conversion of the results obtained in specific gravity determinations to the equivalent percentages of solid matter be inserted in the official methods of analysis. The table referred to in the present methods, and given on page 214 of Bulletin 31, is quite at variance with the tables published in recent works on sugar analysis.

7. After the word "water," page 354, method (c), line 8, make the method read, "filter immediately and finish the determination by one of the methods given below for the determination of the copper contained in the precipitate of cuprous oxid obtained in the determinations of reducing sugars." Transfer all of the remaining portion of the paragraph as indicated below. After Allihn's table, on page 358, make a new heading, which shall read, "Methods for the determination of the copper contained in the precipitate of cuprous oxid obtained in determinations of reducing sugars."

Make subheads as follows:

(a) Method requiring reduction in hydrogen. Here insert the method now forming the last portion of the first paragraph under method (c), page 354.

(b) Electrolytic method by solution in nitric acid, and subsequent evaporation with an excess of sulphuric acid.

(c) Electrolytic method by solution in a mixture of nitric and sulphuric acids.

(d) Electrolytic method by solution in nitric acid.

(e) Volumetric method (adopted provisionally). Here insert the potassium permanganate method.

8. At the close of method (a), under "Estimation of sucrose," page 359, insert, "it must be remembered that a change of 5° in the temperature of the solution between the time of filling the flask to the mark and the time of making the reading will cause a change in volume, which will give rise to an error of approximately 0.1 per cent in the polarization of materials containing from 90 to 100 per cent of sucrose, and an error of approximately 0.05 per cent in the case of materials containing 50 per cent of sucrose."

9. That the method of Clerget as now given in the methods, and the method of Lindet, be stricken from the methods at the meeting of 1896, unless some reason for their retention, now unapparent to your reporter, come to persuade the association to a different view of the value of the method as it now stands.

10. Page 360, method (b), line 6, after the word "added," change to read, "place the flask in a water bath the temperature of which is 70° . The contents of the flask should reach a temperature of 67° to 70° in two or three minutes, when the temperature should be maintained within this limit for exactly five minutes." Cut out the words rendered superfluous by this change.

11. Page 360, line 6, make this line read, " $a-b$ = the algebraic difference between the two polarizations." Change the formula accordingly, and cut out the explanatory clause immediately following the formula.

12. Page 359, immediately after the title "Estimation of sucrose," insert a sub-head, "Optical methods."

13. Page 360, gravimetric method, make this heading coordinate with "Optical methods" and "Optical methods by inversion."

SUBJECTS SUGGESTED AS APPROPRIATE FOR INVESTIGATION DURING THE ENSUING YEAR.

Comparative tests of the pumice-stone method for the determination of water. It is recommended that this study be begun with known solutions of pure carbohydrates, and be extended to impure and mixed solutions after the accuracy of the method has been established in the case of pure materials in the hands of several analysts.

The propriety of making the optical method by inversion read as follows: Determine the polarization before inversion as directed in the method for single polarization. For the reading after inversion, weigh such a quantity of the sample as will yield approximately the quantity of invert sugar which would be obtained by inversion of 13.024 grams of sucrose; dissolve in water, transfer to a 100 cc flask, dilute with water to approximately 75 cc, and finish the determination according to the German official method.

The value of Ost's modification of Soldaini's method for the determination of reducing sugars.

The method of obtaining the weight of copper obtained in determinations of reducing sugars, by solution of the precipitate of cuprous oxid in a solution of ferric sulphate and the titration of the solution with a standard solution of potassium permanganate.

Investigation in regard to the best method for conducting inversions of sucrose by means of invertase and in regard to the factor to be employed when this agent is used in the place of acid in the optical method by inversion.

The accuracy of Gird's gravimeter for weighing out portions of juices and other dilute liquids for polarization. For a description of this instrument, see *Jour. Am. Chem. Soc.*, 1894, **16**, 677.

A comparison of the accuracy of the various grades of Brix spindles offered for sale by apparatus dealers.

A comparison of the accuracy of the graduated glassware offered for sale by apparatus dealers, with the view of prescribing the limits of error allowable in graduated glassware to be used for official work.

A similar comparison of the thermometers offered for sale by the dealers.

The desirability of using the residue obtained in the determination of water by the pumice-stone method, for the determination of ash.

The president stated that the recommendations of the reporter on sugar would go to the committee for action, and then called for the report on tannin.

REPORT ON TANNIN.

By WILLIAM H. KRUG.

In accordance with the instructions of the association, the reporter on tannin this year sent out a sample of extract and two samples of hide powder—No. 1, from Richards & Co., being granular, and No. 2, from Mr. Fiebing, being fibrous. These samples were accompanied by a circular letter giving an outline of the special work desired. There seems to have been a lack of interest, though, and several chemists on whom the reporter relied for extensive and valuable reports failed to send any data whatever. This must be deplored, as I believe that the work has arrived at a stage where some radical changes will be made, and where the utter uselessness of the hide-powder method is proved.

In addition to the regular work done on the provisional method, as modified at the last meeting, the following special work was requested from the analysts.

I. Total solids determination—

Method 1. Dry 5 grams of the extract at 100° until the residue ceases to lose weight.

Method 2. Dry 100 cc of the diluted extract at 100° until the residue ceases to lose weight.

Method 3. Heat good porous pumice stone until all moisture has been driven off. After cooling, cut it into pieces (1) 1 cm. square and (2) smaller particles which pass through a sieve having six meshes to the inch. Cover the bottom of a flat platinum dish of proper size with the small particles, and on these place a layer of the larger pieces. Heat the dish and contents to redness for about fifteen minutes, cool, and weigh. By means of a small pipette with a small nozzle, distribute from a hand flask about 10 grams of the diluted extract evenly over the larger pieces. Dry at 100° until constant weight is obtained. This should be accomplished in a few hours.

II. Tannin estimation—

Make a series of determinations—

(a) Using the three portions of hide powder without intermediate filtration.

(b) Using the hide powder all at once.

The opinion of the various analysts on the best method of filtration was also desired, as well as any additional work which might be suggested during the course of the regular investigation.

Five chemists sent in full reports, while two others reported determinations of the solids.

General table of results.

Analyst.	Total solids.			Soluble solids.	Tanning substances.					
	Meth- od 1.	Meth- od 2.	Meth- od 3.		Method a.		Method b.		Method c. ¹	
					Hide pow- der I.	Hide pow- der II.	Hide pow- der I.	Hide pow- der II.	Hide pow- der I.	Hide pow- der II.
	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>
J. H. Yocum	43.33	43.55	43.38	42.15	16.21	16.78	16.80	17.06
G. A. Kerr	43.38	43.71	41.71	14.80	10.54	14.34	14.70
B. D. Westenfelder	44.52	44.24	43.47	43.19	17.29	17.34	17.20	17.40
J. L. Fiebing.....	41.70	41.70	41.65	38.10	15.70	15.70	15.30	15.30	17.10	17.10
W. H. Krug.....	43.11	42.71	45.00	42.35	15.73	16.02	14.98	14.65	15.87	16.41
J. S. Carman	43.52	42.68	40.87
F. L. Johnson.....	43.25	42.72	43.09
J. N. Hurty	42.67	42.98	41.60	13.58	16.08	16.54	16.54
Means	43.16	42.99	43.39	41.42	15.72	15.86	15.36	15.11	16.31	16.52
Difference between maxi- mum and minimum.....	2.82	2.54	4.65	5.09	3.71	6.80	2.86	2.70

¹ Provisional method.

Only three chemists sent in data on the hide powder. These showed that neither sample came within the requirements of the association.

Residue from 100 cc of final filtrate, 10 grams hide powder washed three times with 200 cc of distilled water.

Analyst.	No. 1.	No. 2.
	Per cent.	Per cent.
J. H. Yocum ¹	0.1015	0.0428
Wm. H. Krug0211	.0288
G. A. Kerr0450	.0340
J. N. Hurty0230	.0170

¹ Mr. Yocum used only 9 grams of hide powder.

The separate reports contain much that is of interest, and I therefore give extracts from them.

Mr. Yocum characterized hide powder No. 1 as being one that without great care would give wrong results, as it contains much soluble matter. He also analyzed the extract with two other hide powders, the first being used dry, the second, an old sample, washed in the customary manner. The first gave 29.34 per cent nontannins (12.81 per cent tanning substances), and as this hide powder contained 0.0800 gram soluble matter, which, when deducted from the residue, gives 25.22 per cent nontannins (16.93 per cent tanning substances), it is quite evident that all this soluble matter must have practically passed into the final liquid. The second hide powder, about two years old, gave 27.96 to 28.02 per cent nontannins (14.16 per cent tanning substances), which low result was no doubt due both to poor absorptive power and solution of soluble matter from the hide. Mr. Yocum found that on dissolving the extract in cold water more insoluble matter was left behind. Thus, by the usual method the insoluble matter or reds was 1.27 per cent (42.15 per cent soluble solids), while solution in cold water (17°) gave 2.15 per cent (41.27 per

cent soluble solids). He examined the hide powders used in his work with the following results:

Weight of residues obtained.

Kind of hide powder.	9 grams of hide powder washed 3 times with 200 cc of water; 100 cc of final filtrate evaporated.	30 grams of this (=8 grams dry) shaken with another 200 cc of water for 15 minutes, and 100 cc evaporated.	9 grams of hide powder washed once with 200 cc of water and 100 cc of filtrate evaporated.
No. 1.....	0.1015	0.0040	0.2840
No. 2.....	.0428	.0060	.1480
Laboratory.....	.0197	.0040	.0800

All these figures throw out the two hide powders sent. The following figures were obtained with the hide powder used in the laboratory:

Per cent.

Nontannins by official method..... 25.92 = 16.23 tanning substances.

Nontannins, using all hide powder at once, shaken twenty minutes..... 25.89 = 16.26 tanning substances.

Nontannins, using hide powder dry..... 29.34 = 12.81 tanning substances.

Mr. Yocum thinks that the solution is best filtered by passing 250 to 300 cc through paper before taking the amount required for analysis, and entirely discarding that which passes through first.

Mr. Kerr, associate reporter on tannins, became thoroughly disgusted with hide powder during the work, and subsequently wrote me that he was using a new method suggested by Mr. Stürcke, of Chicago. This consisted of forcing the tannin liquor through a column of asbestos impregnated with mercuric oxid. In his final report he sends the following results obtained on the official extract with this method:

Results with mercuric oxid method.

Dilution.	Amount of reagent used.	Soluble solids.	Insoluble matter (reds).	Tanning substances.
		<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
5.093 grams, 1,000 cc.....	2 grams HgO and 5 grams asbestos.	41.80	1.90	23.20
20.36 grams, 1,000 cc.....	do	41.74	1.53	22.79
Do.....	2 grams HgO and 10 grams asbestos.	41.74	1.53	23.34

Mr. Kerr wrote that in no case could either mercury or tannin be found in the final filtrate, and that he was therefore using this method altogether in his laboratory.

Mr. Westenfelder writes that he used both filter paper and asbestos fiber with filter pump, and found no appreciable difference in the results for total soluble matter, though the pumps filtered much more rapidly. He had considerable difficulty in filtering the nontannin solution from the hide powder, and obtained the best results by filtering through the hide powder which had been shaken up with the liquid.

Mr. Fiebing finds it necessary to use the hide powder in three separate portions, and gives the following figures in proof: Official extract, per cent nontannins: (a) Using three portions of hide powder without intermediate filtration, 22.4 per cent; (b) using hide powder all at once, 22.8 per cent; (c) using hide powder in two portions with intermediate filtration, 21.7 per cent; (d) using the hide powder in three portions with intermediate filtration, 21 per cent. Fresh hemlock liquor, nontannins: (a) Four portions of hide powder with intermediate filtration, 1.95 per cent;

(b) three portions of hide powder with intermediate filtration, 2 per cent; (c) three portions without intermediate filtration, 2.10 per cent. Leached hemlock bark, non-tannins: (a) Three portions of hide powder with intermediate filtration, 1.58 per cent; (b) three portions of hide powder without intermediate filtration, 1.68 per cent.

DISCUSSION OF RESULTS.

On comparing this year's results with those of last year, one thing is immediately very evident, and that is that the discrepancies are greater than ever. The figures obtained by the various analysts for total solids agree fairly well with the exception of those reported by Mr. Fiebing. The column "Soluble solids" shows a great variation, and it seems to me that one source of the trouble we have experienced lies here. Mr. Yocum's work on the insoluble matter obtained by hot and cold solution, shows that variations in the temperature of the water used can cause considerable variation in the amount of soluble solids. I did some work on this point and obtained the following figures, which confirm those of Mr. Yocum:

[Per cent soluble solids.]

10 grams extract dissolved in cold water made up to 500 cc.	10 grams extract dissolved in water at 80° and made up to 500 cc when cool.
40.46	42.46
40.42	42.23
40.42	-----

Here is a difference of almost 2 per cent, which, when the extract is properly dissolved, will go to the credit of the hide powder. I do not mean to say by this that more care in the manner of dissolving the sample will insure better or more concordant results. I do not think that such results can be obtained with hide powder, and that we will sooner or later be forced to discard it. The differences between the results obtained by different analysts are too great to be ascribed to anything but the reagent itself. The manner of carrying out the method could not differ so radically among chemists as to account for these discrepancies. The results also indicate that there is no radical difference between the two hide powders, i. e., excepting the result obtained by Mr. Kerr in using all the hide powder at once.

Shortly after the last meeting, Mr. Kerr wrote to various firms asking for samples of their best hide powder. He received a number of samples, which he analyzed. Unfortunately, I do not have the figures at hand, but his report showed the granular powder from Richards & Co. and the fibrous powder made by Mr. Fiebing to come within the requirements of the association. On the strength of this, these powders were used, and the subsequent results show the unreliability of hide powder in general. It is evidently impossible to obtain two samples of hide powder even approximately similar, and the differences between the residues from 100 cc of the final washing of the powder shown in Table 2 indicate that this variation extends even to the small samples sent out. Such being the case, I do not see how we can place any reliance on the reagent or results obtained by it. I think the work of the last two years shows this very plainly, and indicates that the realization of a good, reliable method lies in another direction. I do not at this time venture to say where we shall turn for a new method, although I think that the experimental work which I will now discuss seems to point a way to get out of the dilemma. As I stated above, Mr. Kerr, during the progress of our joint work, sent me a description of the mercuric-oxid method as he was using it, and also an apparatus already charged and ready for use. I made a number of estimations by this method, but the results varied so much that I do not consider them worth reporting. Subsequent developments showed

that my failure was mainly due to the variety of asbestos I used, though at the time I ascribed it to other causes, such as unequal packing and distribution of HgO , imperfect contact, etc. This work, however, suggested another line of investigation to me, which I will discuss briefly. Failing to get good results by percolation, I turned to find another method of using the mercuric oxid, and finally decided to apply it exactly as the hide powder is now used. I subsequently extended the work to several other oxids. It was evident at the beginning that considerably more time would be consumed in absorbing the tannin in this manner, and a number of experiments were made to determine the time limit. In all cases where upon filtration after shaking a certain length of time it was found that combination was incomplete, the mixture was allowed to stand until this was accomplished. It was thus found that with mercuric and magnesium oxids it was best to shake about four hours and then let the mixture stand over night, when it would be ready for filtration. With lead oxid the process required two days, after being shaken four hours, and the mixtures with zinc oxid stood a week before the tannin was totally absorbed.

The last two oxids were therefore rejected as requiring too much time, although the analyses made with them are given for comparison. The diluted extract gave in 25 cc as a mean of three determinations 0.0113 gram ash, containing 0.0006 gram MgO . The ash determinations were made as a check on the amount of oxid dissolved during analysis.

Experiments with ZnO .

Method.	ZnO used.	Diluted extract used.	Filtrate evaporated.	Weight of residue.	Tannin in extract.	Ash in residue.	ZnO in ash.
	<i>Grams.</i>	<i>cc.</i>	<i>cc.</i>	<i>Gram.</i>	<i>Per cent.</i>	<i>Gram.</i>	<i>Gram.</i>
Shaken 4 hours, stood over night....	2	75	25	0.1095	20.45	0.0125	0.0008
Do.....	2	75	25	.1174	18.87	.0147	.0016
Shaken 4 hours, stood 1 week.....	2	75	25	.1049	21.37	.0095
Do.....	2	75	25	.1029	21.97	.0103	.0030
Do.....	2	75	25	.1029	21.97	.0100	.0020

The first two filtrates gave a faint reaction for tannin, but were run through so as to compare the results with those obtained with other oxids during the same length of time. The last three gave no test for tannin, and agree fairly well. They are low, compared with lead and mercury oxids, and agree better with those obtained with magnesium oxid. The amount of zinc oxid dissolved is too small to affect the accuracy of the analysis, and the only objection to the use of this oxid is the slow action, which makes it impracticable in a laboratory when rapid work is desired.

Experiments with lead oxid, PbO .

Method.	PbO used.	Diluted extract used.	Filtrate evaporated.	Weight of residue.	Tannin in extract.	Weight of ash from residue.	Ash contained PbO .
	<i>Grams.</i>	<i>cc.</i>	<i>cc.</i>	<i>Gram.</i>	<i>Per cent.</i>	<i>Gram.</i>	<i>Gram.</i>
Shaken $3\frac{1}{2}$ hours, stood 2 days.	4	75	25	0.0738	27.59	0.0111	0
Do.....	4	75	25	.0754	27.27	.0092	0
Do.....	4	75	25	.0706	28.23	.0105	0

None of these gave a reaction for tannin. The results were higher than with any oxid used. The objection to lead oxid is the length of time required for complete absorption.

Experiments with magnesium oxid.

Method.	MgO used.	Diluted extract used.	Filtrate evapo- rated.	Weight of residue.	Tannin in ex- tract.	Weight of ash in residue.	MgO in ash.
	<i>Grams.</i>	<i>cc.</i>	<i>cc.</i>	<i>Gram.</i>	<i>Per cent.</i>	<i>Gram.</i>	<i>Gram.</i>
Shaken 2½ hours, stood over night.....	2	75	25	0.1134	19.67	0.0209	0.0055
Do.....	2	75	25	.1028	21.79	.0195	.0042
Do.....	2	75	25	.1230	17.75	.0232	.0052
Do.....	2	75	25	.1246	17.43	.0247	.0058
Stood 24 hours, occasional shaking.....	2	75	50	.2063	21.72	.0252	.0074
Do.....	2	75	50	.2061	21.74	.0244	.0076
Do.....	2	75	25	.1157	19.21	.0213	.0044
Do.....	2	75	25	.1114	20.07	.0205	.0038
Stood 48 hours, occasional shaking.....	2	75	50	.1941	22.94	.0326	.0064
Do.....	2	75	50	.1959	22.76	.0339	.0070
Shaken 3½ hours, stood over night.....	2	75	50	.2165	20.70	.0349	.0102
Do.....	2	75	50	.2191	20.44	.0355	.0111
Do.....	2	75	50	.2179	20.56	.0359	.0115

This table shows that a considerable amount of the oxid is dissolved and passes into the filtrate, increasing the weight of the residue and correspondingly lowering the tannins. This error does not seem to be constant, so that no correction can be made for it.

Experiments with mercuric oxid (yellow).

Method.	HgO used.	Diluted extract used.	Filtrate evapo- rated.	Weight of residue.	Tannins in extract.	Ash in residue.	HgO in ash.
	<i>Grams.</i>	<i>cc.</i>	<i>cc.</i>	<i>Gram.</i>	<i>Per cent.</i>	<i>Gram.</i>	<i>Gram.</i>
Stood 48 hours, occasional shaking.....	4	75	25	0.0833	25.69	0.0070	0
Do.....	4	75	25	.0829	25.77	.0077	0
Do.....	4	75	25	.0829	25.77	.0071	0
Shaken 1½ hours, stood over night.....	4	75	25	.0842	25.51
Shaken 2 hours, stood over night.....	4	75	25	.0867	25.01
Shaken 3½ hours, stood over night.....	4	75	25	.0863	25.09	.0081	0
Do.....	4	75	25	.0860	25.15	.0080	0
Shaken 4 hours, stood over night.....	4	75	25	.0839	25.57	.0084	0
Do.....	4	75	25	.0849	25.37	.0065	0
Do.....	4	75	20	.0638	26.41	.0065	0
Do.....	4	75	20	.0692	25.05	.0103	0
Do.....	4	75	20	.0682	25.29	.0094	0
Do.....	4	75	25	.0863	25.09	.0083	0
Do.....	4	75	25	.0849	25.37	.0097	0
Do.....	4	75	25	.0842	25.51	.0084	0

These analyses show that even though the conditions may be varied fairly concordant results can be obtained with HgO as long as care is taken to insure the complete absorption of the tannin before filtering. The end of the reaction may be easily observed with all the oxids used, and especially so with HgO, since, when it is

reached, the oxid no longer sinks to the bottom after shaking, but the whole mass partially gelatinizes and becomes a dirty brown in color. A clear filtrate, free from tannin and mercury, can then be easily obtained. The results in the ash column indicate that a certain amount of the ash present in the extract is held back, but this error is quite constant and so small as to have little influence on the result. Although the time required for the analysis of a tanning liquor by this method is somewhat longer than with hide powder, still the uniform results obtained more than compensate for this, and at the most an analysis will not take more than two days. A number of analyses can be made at a time by adapting a shaker, so as to hold several 100 cc sugar flasks, which are of a convenient size for this work.

After I had commenced this work just reviewed, Mr. Kerr wrote me that he had discovered that the asbestos which he had been using absorbed tannin completely. He sent a sample, which I tested and found to be a true absorbent, just as he had stated. A quantity which I subsequently ordered from Richards & Co., in Chicago, also possesses this remarkable property, which I have been unable to explain, except by the presence of an excess of some oxid, such as MgO , which combines with the tannin. It was too late to do much work on this, and I was only able to make a few analyses, of which I report the last two, since they agree very well. Each analysis required 45 grams asbestos wool in four portions of 10 grams each and one portion of 5 grams, when the tannin was found to be absorbed, the residual liquor being only slightly colored and giving no reaction with ferric chlorid. The two analyses gave 18.66 and 18.23 per cent tanning substances, respectively, results which are somewhat higher than those obtained with hide powder and lower than those given by mercuric oxid.

This difference in results suggests another difficulty which confronts us. If the asbestos absorbs nothing but tannin, then mercuric oxid must combine with other substances which are not tannins, and we naturally ask whether these nontannins are also absorbed by the hide in the process of leather making, and should be included in the valuation of an extract. These points need further investigation, and I would suggest that the work of the next year be concentrated on them, with the view of solving them as nearly as possible.

The president called for papers relating to the subject, and for the discussion of the report.

Mr. GOSS. I have never done any work on tannin, but it seems to me that the hide-powder method should certainly be well considered before being discarded. While it is true that the method may give poor results for the year, it is likewise true that we have the same variations in the substances we are trying to tan.

Mr. KRUG. German chemists have come to the conclusion that when their results are off, it is the fault of the powder. I don't mean to drop hide powder, but I think another method should be tested. The hide powder gives most variable results. A difference of 7 per cent can not be ascribed to differences in manipulation of the chemist, because the directions are strict and he ought to get within 0.5 of 1 per cent. A difference of 7 per cent can not be accounted for otherwise except by the fault of the powder.

Mr. HUSTON. Is there any further discussion?

Mr. MITCHELL. The tannin chemists have called us to account for determining tannic acid rather than the tanning power of the extract, and we have come to use the hide-powder method as one giving approximately the results obtained. I think we have two things to determine,

one the variations of the bark and the other of the substances to be tanned.

Mr. KRUG. I would say concerning the official extract that we use, that if any chemist should report to the firm that is using it that it had only 17 per cent of tanning substance the firm would call him to account for it. They know it has more than that. Two chemists reporting, one 10 per cent and the other 17 per cent, would be called to account.

Mr. MITCHELL. I think on hemlock bark the hide powder has had its best results and obtained its greatest hold.

Mr. Goss called attention to a method in which permanganate of potash is used.

Mr. Krug remarked that the substances which tan leather are really not all tannic acid. He said there were other substances which entered into the composition of leather which are not tannic acid, and must be taken into consideration.

Mr. Goss said that all general methods were along the same line as the hide-powder method.

Mr. Huston then called for the recommendations of the reporter.

Mr. Krug recommended that the work with mercuric oxid be taken up by the association the coming year, and that the hide-powder method should also be continued. No recommendations as to changes in methods are deemed advisable.

The president then called for the report of the committee on changes of methods on nitrogen.

Mr. Lindsey reported that the committee recommended the adoption of the Ulsch method as modified by Street, using 5 grams of magnesium oxid, as a proposed official method, to be voted upon for adoption next year.

The recommendation was adopted.

Mr. Lindsey then recommended the zinc-iron method as a proposed official method, to be voted upon for adoption next year, for determination of nitrates.

The recommendation was voted upon and adopted.

Mr. LINDSEY. The committee recommends that we print the method for the determination of ammonia by distilling with magnesium oxid, and that it be adopted at the present time.

Mr. WHEELER. Our law does not require it, but we always use this method.

Mr. LINDSEY. We suggest to the reporter the further trial of the Fassbender method with a view to possible adoption next year.

The motion was carried.

The president then called for the report of the committee on changes in methods of sugar analysis.

Mr. LINDSEY. The committee recommends the adoption of the recommendations as a whole, and that the arrangement and editing of the same be referred to the present reporter and to Secretary Wiley.

The recommendation was adopted.

The president then called for remarks by President elect Ross.

Mr. Ross said he had not had time to make a list of reporters and committees and had not been able to complete the work of conference with reporters on some matters. His appointments would be filed with the secretary at a later date.

Mr. MYERS. In the adoption of the resolution recognizing the courtesy extended to us by the authorities of the Smithsonian Institution and the National Museum, I believe we omitted to include also the courtesy extended by the United States Department of Agriculture. I therefore move that the secretary be instructed to communicate to the Secretary of Agriculture our appreciation of his helpfulness in connection with our work.

Mr. WILEY. I suggest that the Assistant Secretary also be included. The motion was carried.

Mr. Myers moved that the thanks of the association be extended to the chairman for the able manner in which he presided over the meeting.

The motion (Mr. Myers acting as chairman) was carried, and the retiring president thanked the association for the courtesy.

Mr. WILEY. One matter I would like to call up. I suggest that the reporter on soil analysis for next year be instructed to bring the subject of the mechanical analysis of soils before the members of the association, and to get an expression of opinion in regard to methods.

The recommendation was adopted.

Mr. Wiley remarked that the members of the executive committee would be glad to have some expression in regard to the time of meeting.

The PRESIDENT. The matter of the time for the next meeting is up for consideration.

Mr. WHEELER. I would prefer to have the meeting when it is cooler.

Mr. Lindsey said he had suggested to some of the members that the meeting be held at the same time, or two or three days before, the Convention of Agricultural Colleges and Experiment Stations. He thought there were many who might desire to attend both associations. He said many objections had been made to the proposition. He also suggested that members coming from the cooler parts of the country could contribute more strength and intelligent opinion to the meetings if they were held a little later.

Mr. Wheeler agreed in this opinion.

Mr. Persons thought it might be well to hold the meetings at the same time as the Convention of Agricultural Colleges and Experiment Stations.

Mr. HUSTON. I do not think it advisable to meet with the Association of Agricultural Colleges and Experiment Stations.

Mr. MYERS. I agree with the president. The proceedings of the two conventions are of an entirely different character and would conflict with one another by coming together. The proper function of the

agricultural colleges and experiment stations is the discussion of executive matters and questions of organization. The proper function of this association is the discussion of methods and scientific questions, and we do not want to get these things mixed up. It makes no difference to me when the meeting is held, but it should be held early enough so that chemists who have charge of fertilizer inspection in the South could get hold of the methods in time to use them for the year. November makes it too late for that. I don't think it desirable to connect ourselves in any way with the other association.

Mr. Rawls said he preferred Washington as the place of meeting. It looked better to the authorities. He said that in Florida they commence fertilizer work early, and like to get the bulletins as early as possible.

Mr. HUSTON. It makes no difference to me when the meeting is held. Does the association wish to fix the place of meeting?

Mr. LINDSEY. I think the association voted to hold the meetings in Washington, and this has not been changed.

Mr. MYERS. I move the matter be referred to the executive committee, with power to act.

After some discussion, the motion was withdrawn, and the chairman called for the report of the committee on changes in methods of analysis of distilled liquors.

Mr. LINDSEY. The committee recommends the following in regard to distilled liquors: That in the alcohol determinations the use of the mercury valve be discontinued.

Recommendation adopted.

Mr. LINDSEY. That in the glycerol determination there be added to the method after the words "water oven" the following: "and weighed, the ash determined in it, and its weight deducted from that of the weighed residue."

Recommendation adopted.

That the directions for the determination of alcohol be made to read as follows:

II.—DETERMINATION of ALCOHOL—

(a) In fermented liquors.

(1) *By weight*.—One hundred cc of the liquor are measured into a flask of from 250 to 300 cc capacity, 50 cc of water added, the flask attached to a vertical condenser by means of a bent tube, and 100 cc distilled. The specific gravity of the distillate is determined as in 1. The distillate is also weighed, or its weight calculated from the specific gravity. The corresponding percentage of alcohol by weight is obtained from the appended table, and this figure multiplied by the weight of the distillate, and the result divided by the weight of the sample taken, gives the per cent of alcohol by weight.

(2) *By volume*.—The percentage of alcohol by volume of the liquor is the same as that of the distillate, and is obtained from the appended table.

(b) In distilled liquors.

(1) *By weight*.—About 30 grams of the liquor are weighed, diluted to 150 cc, 100 cc distilled, and the per cent of alcohol by weight determined as under fermented liquors.

(2) *By volume.*—The percentage of alcohol by volume in the distillate is obtained from the appended table, this figure divided by the volume of the liquor taken for the determination (calculated from the specific gravity), and the result multiplied by 100.

Recommendations adopted.

The president then asked if there was any further business before the meeting.

Mr. Lindsey asked if there were no associate reporters to be appointed.

Mr. HUSTON. The appointment of reporters, of abstract committee, and of the editing committee is in the hands of the president elect.

Mr. Ross then announced the appointment of reporters and associate reporters (see list of officers).

The president thereupon declared the convention adjourned.

OFFICERS, REPORTERS, AND COMMITTEES OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS OF THE UNITED STATES FOR 1895-96.

PRESIDENT.

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VICE-PRESIDENT.

Mr. WILLIAM FREAR, State College, Pa.

SECRETARY.

Mr. H. W. WILEY, Washington, D. C.

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Mr. H. J. WHEELER, Kingston, R. I.

Mr. F. W. TRAPHAGEN, Bozeman, Mont.

REPORTERS.

Phosphoric acid.—Mr. H. B. McDONNELL, College Park, Md.

Nitrogen.—Mr. J. P. STREET, New Brunswick, N. J.

Potash.—Mr. A. L. WINTON, New Haven, Conn.

Soils and ash.—Mr. A. GOSS, Mesilla Park, N. Mex.

Dairy products.—Mr. L. L. VAN SLYKE, Geneva, N. Y.

Foods and feeding stuffs.—Mr. J. B. LINDSEY, Amherst, Mass.

Fermented and distilled liquors.—Mr. W. D. BIGELOW, Washington, D. C.

Sugar.—Mr. H. H. NICHOLSON, Lincoln, Nebr.

Tannin.—Mr. G. A. KERR, Columbus, Ind.

ASSOCIATE REPORTERS.

Phosphoric acid.—Mr. L. H. MERRILL, Orono, Me.

Nitrogen.—Mr. R. J. DAVIDSON, Blacksburg, Va.

Potash.—Mr. W. L. HUTCHINSON, Agricultural College, Miss.

Soils and ash.—Mr. W. G. BROWN, Washington, D. C.

Dairy products.—Mr. C. L. PENNY, Newark, Del.

Foods and feeding stuffs.—Mr. F. W. MORSE, Durham, N. H.

Fermented and distilled liquors.—Mr. W. C. BLASDALE, Berkeley, Cal.

Sugar.—Mr. L. W. WILKINSON, Audubon Park, New Orleans, La.

Tannin.—Mr. B. D. WESTENFELDER, Cincinnati, Ohio.

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Mr. C. L. PARSONS, Durham, N. H.

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Mr. A. M. PETER, Lexington, Ky.

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Mr. W. H. KRUG, Washington, D. C.

Mr. B. W. KILGORE, Raleigh, N. C.

Mr. E. H. FARRINGTON, Madison, Wis.

Mr. J. L. BEESON, Audubon Park, New Orleans, La.

COMMITTEE ON PURE FOOD LEGISLATION.

Mr. H. W. WILEY, Washington, D. C., chairman.

Mr. H. A. HUSTON, La Fayette, Ind.

Mr. JOHN A. MYERS, Morgantown, W. Va.

Mr. A. S. MITCHELL, Milwaukee, Wis.

CONSTITUTION OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.

(1) This association shall be known as the Association of Official Agricultural Chemists of the United States. The objects of the association shall be (1) to secure uniformity and accuracy of the methods, results, and modes of statements of analysis of fertilizers, soils, cattle foods, dairy products, and other materials connected with agricultural industry; (2) to afford opportunity for the discussion of matters of interest to agricultural chemists.

(2) Analytical chemists connected with the United States Department of Agriculture, or with any State or national agricultural experiment station or agricultural college, or with any State or national institution or body charged with official control of the materials named in section 1, shall alone be eligible to membership, and one such representative for each of these institutions or boards, when properly accredited, shall be entitled to enter motions or vote in the association. Only such chemists as are connected with institutions exercising official fertilizer control shall vote on questions involving methods of analyzing fertilizers. Any person eligible to membership may become a member at any meeting of the association by presenting proper credentials and signing this constitution. All members of the association who lose their right to such membership by retiring from positions indicated as requisite for membership shall be entitled to become honorary members, and to have all privileges of membership save the right to hold office and vote. All analytical chemists and others interested in the objects of the association may attend its meetings and take part in its discussions, but shall not be entitled to enter motions or vote.

(3) The officers of the association shall consist of a president, a vice-president, and a secretary, who shall also act as treasurer; and these officers, together with two other members to be elected by the association, shall constitute the executive committee. When any officer ceases to be a member by reason of withdrawing from a department or board whose members are eligible to membership his office shall be considered vacant, and a successor may be appointed by the executive committee, to continue in office till the annual meeting next following.

(4) There shall be appointed by the president, at the regular annual meeting, a reporter and associate reporter for each of the subjects to be considered by the association.

It shall be the duty of these reporters to prepare and distribute samples and standard reagents to members of the association and others desiring the same; to furnish blanks for tabulating analyses, and to present at the annual meeting the results of work done, discussion thereof, and recommendations of methods to be followed.

(5) The special duties of the officers of the association shall be further defined, when necessary, by the executive committee.

(6) The annual meeting of this association shall be held at such place as shall be decided by the association, and at such time as shall be decided by the executive committee, and announced at least three months before the time of meeting.

(7) No changes shall be made in the methods of fertilizer analyses, except by unanimous consent, until an opportunity shall have been given all official chemists having charge of fertilizer work to test the proposed changes.

(8) Special meetings shall be called by the executive committee when in its judgment it shall be necessary, or on the written request of five members; and at any meeting, regular or special, seven enrolled members entitled to vote shall constitute a quorum for the transaction of business.

(9) The executive committee will confer with the official boards represented with reference to the payment of expenses connected with the meetings and publication of the proceedings of the association.

(10) All proposed alterations or amendments to this constitution shall be referred to a select committee of three at a regular meeting, and after report from such committee may be adopted by the approval of two-thirds of the members present entitled to vote.

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